JOURNAL OF

CHEMICAL EDUCATION

VOLUME 30 | December 1953 | NUMBER 12

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Nephelometry . . the newest analytical tool

Exact measurement of suspended particles without filtering, washing, drying or weighing

Nephelometry is a short way to ...

Directly measure and evaluate the clarity of liquids

One of the earliest industrial applications of Coleman Photo-Nephelometers was made by distillers of whiskies. Evaluation of filters and filter media and control of haze in the finished whiskey is now a-standard procedure throughout this industry. Producers of beer and wines soon followed suit.

Measurement and control of the clarity and sterility of parenterals is an important one and includes such items as: Penicillin, Streptomycin, Dihydrostreptomycin Neomycin Sulfate, Vitamin Solutions.

Perform rapid quantitative analysis by measuring precipitates in their original environment

Purity of industrial waters and other liquids is easily evaluated with the Nephelometer, especially at very low concentrations. For example: Electric generating plants now use Coleman Nephelometers for the evaluation and control of feed waters for high pressure boilers. Control is accomplished by Nephelometric measurement of calcium (Range 0.0—0.5 PPM) in the feed water.

Measure suspensions which cannot conveniently be separated for analysis

In bacteriology the study of the effects of nutrients and inhibitors on growth rates of bacteria has been given new impetus and significance by the simplicity and precision of the Nephelometric method. These studies include a wide variety of bacterial types, including: Leptospira, Actinomyces Bovis, Tubercle Bacilli, Esch. Coli, Staphylococci.

The Nephelometer is useful in determination of butter fat content in dairy products, and has similarly been helpful in assay of cholesterol in blood chemistry.

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COLEMAN MODEL 7 NEPHELOMETER for nephelometry only — ask for Bulletin B-213 • **COLEMAN MODEL 9 NEPHO-COLORIMETER** for colorimetry and nephelometry — ask for Bulletin B-215

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For variable speed stirring action within either closed or open vessels

- **Now offered either with enclosed rheostat or with separate rheostat for control at a distance**
- **With stirring bars sealed in either Pyrex brand glass or Kel-F plastic**

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MAGNETIC STIRRING APPARATUS, A.H.T. Co. Specification. A compact, quiet-running apparatus which utilizes a rotating field of magnetic force to induce variable speed stirring action *within either closed or open vessels.* Now offered in two executions, i.e. with either enclosed rheostat, which will facilitate manipulation in some assemblies; or with separate rheostat for control of speed at a distance of approximately 30 inches from stirrer.

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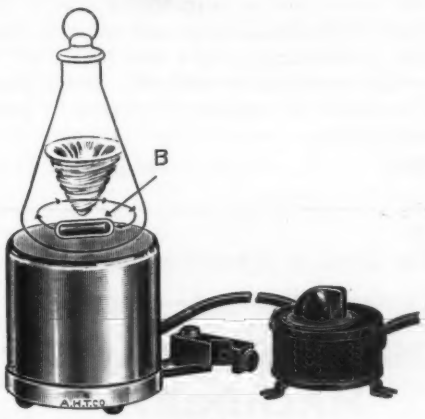

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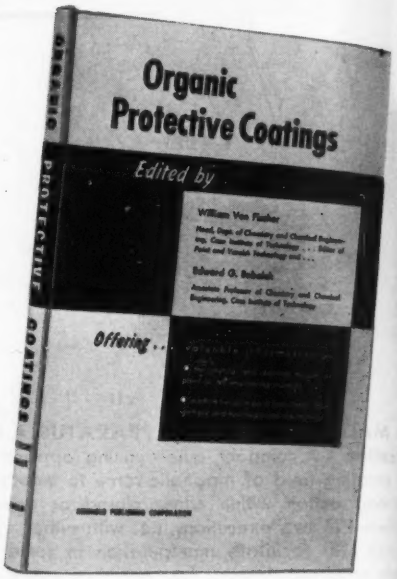

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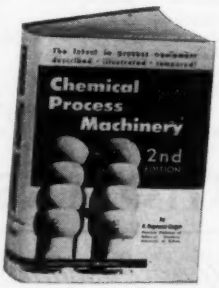

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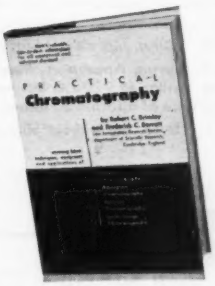

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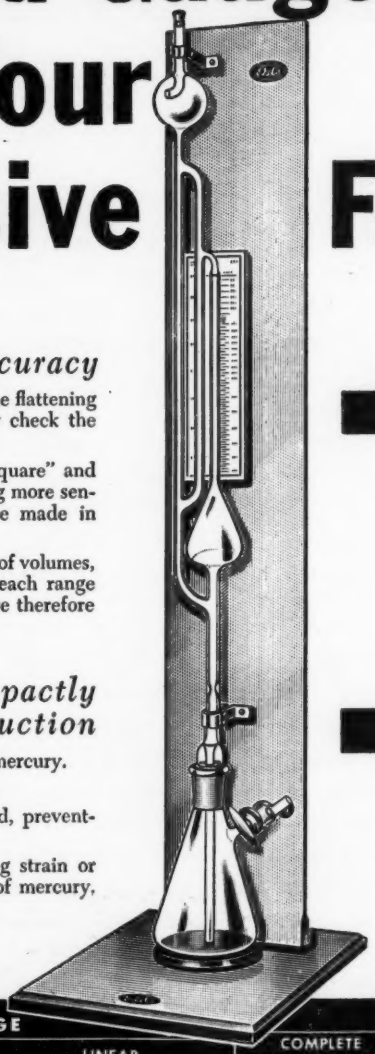

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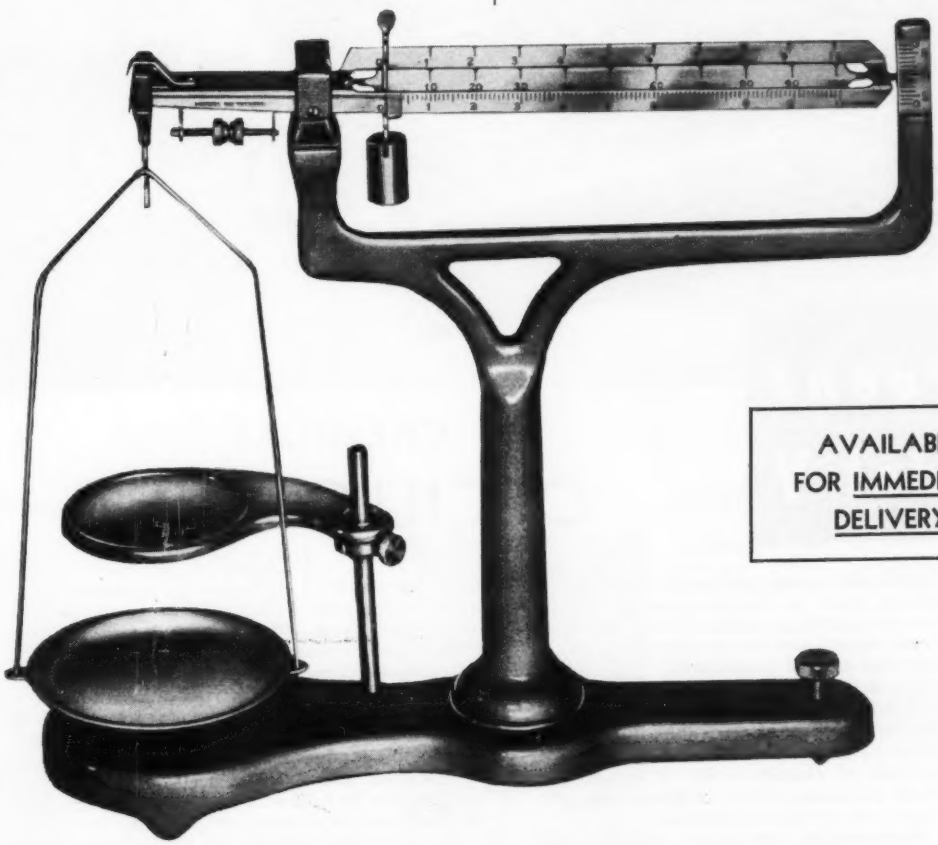

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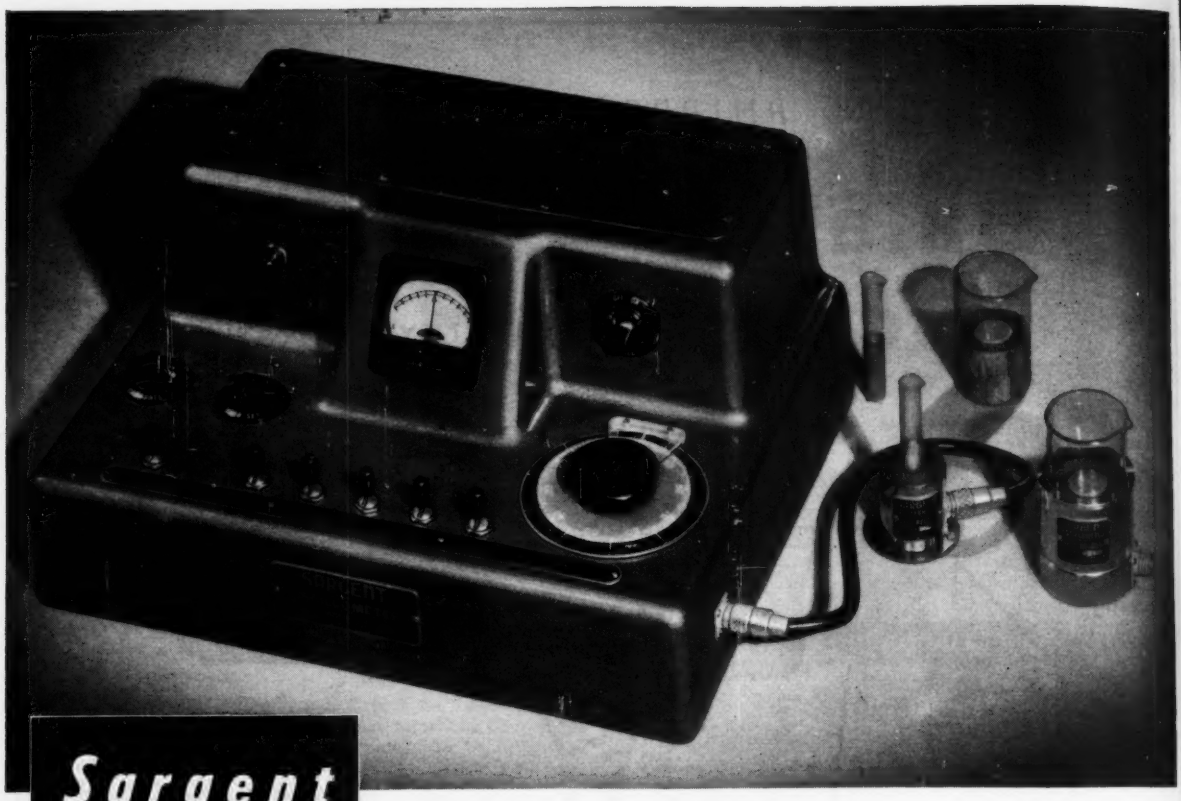

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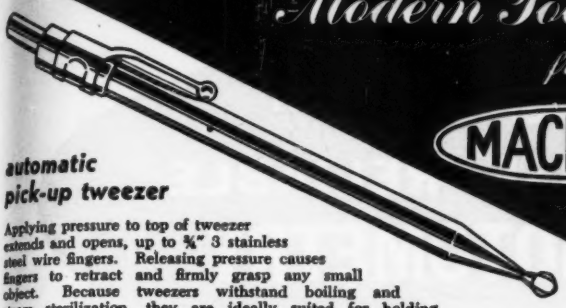

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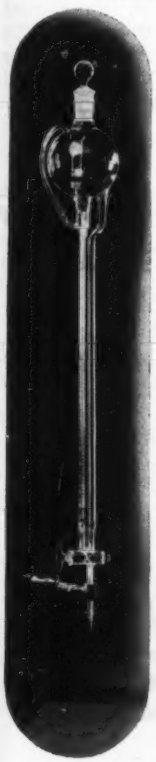

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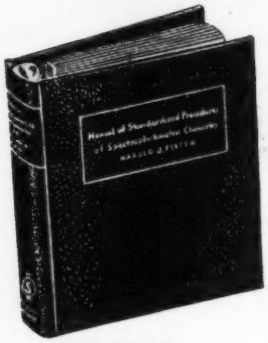

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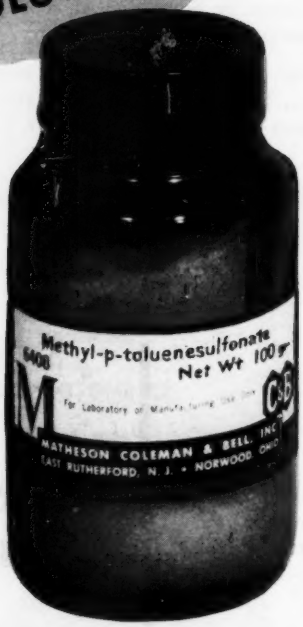

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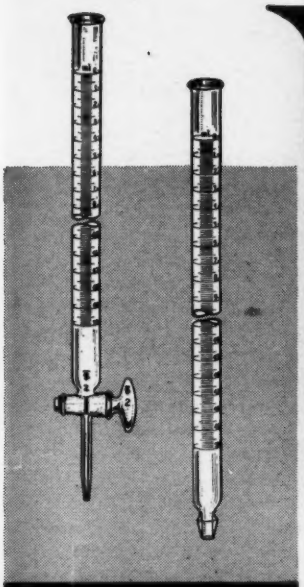

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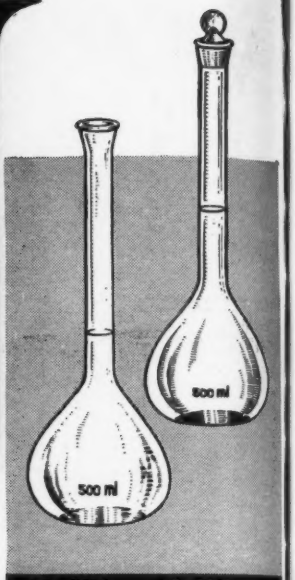

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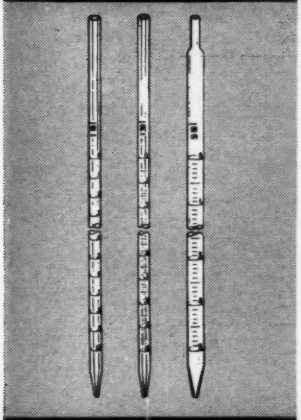

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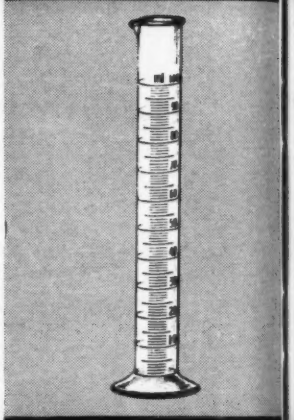

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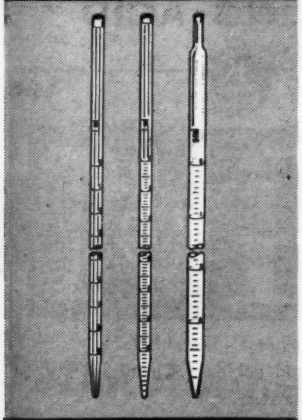

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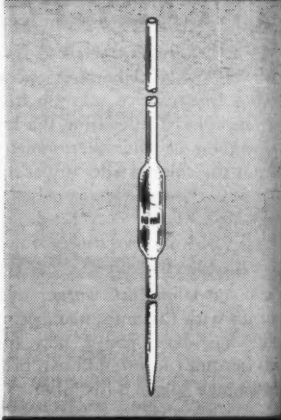

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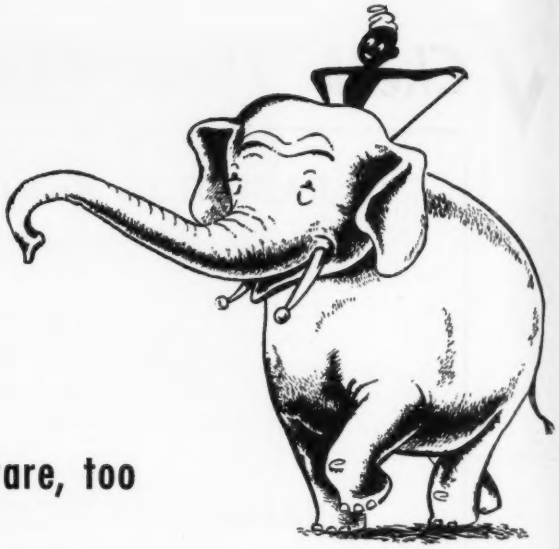

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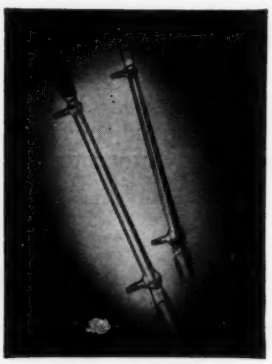

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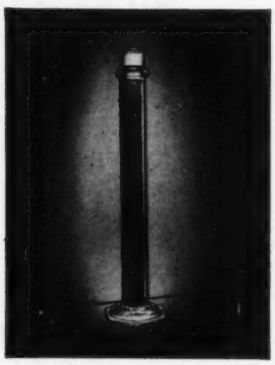

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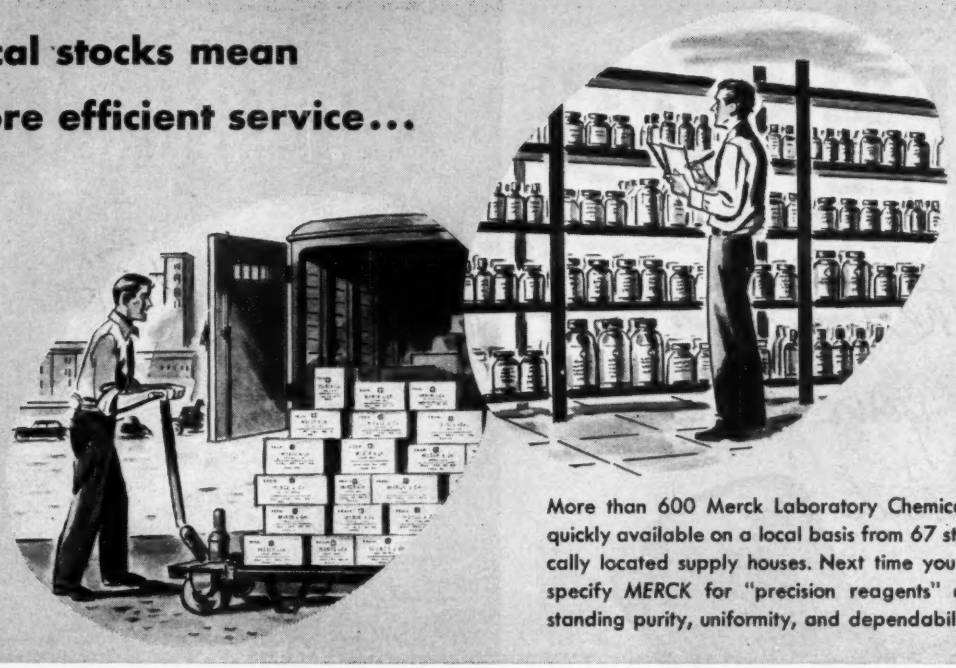

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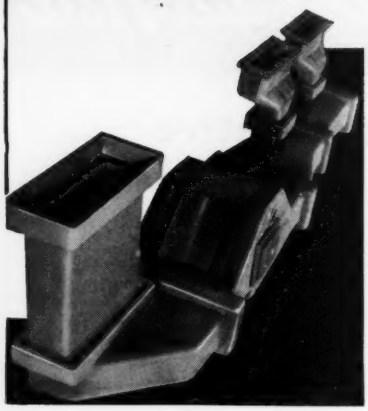

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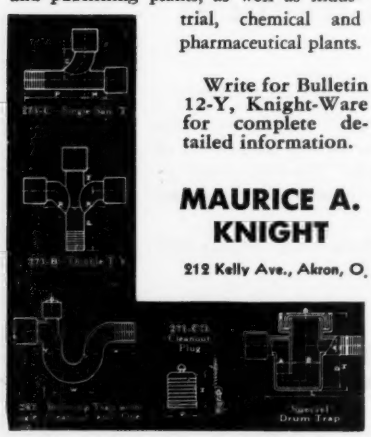

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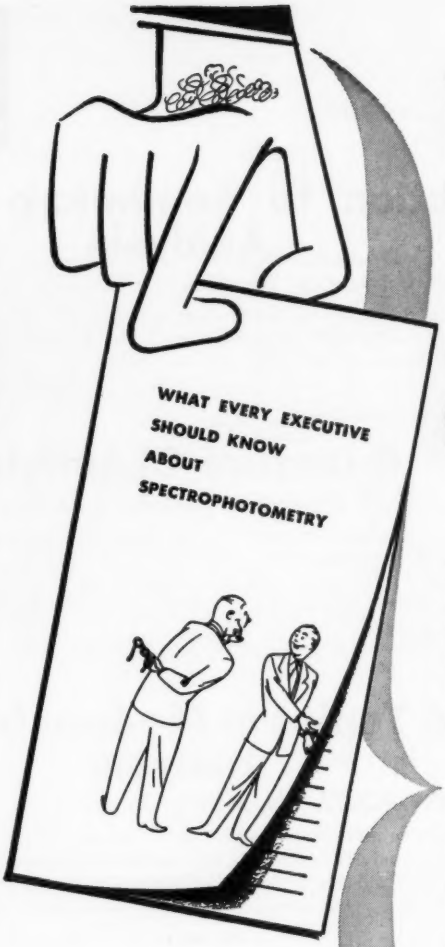

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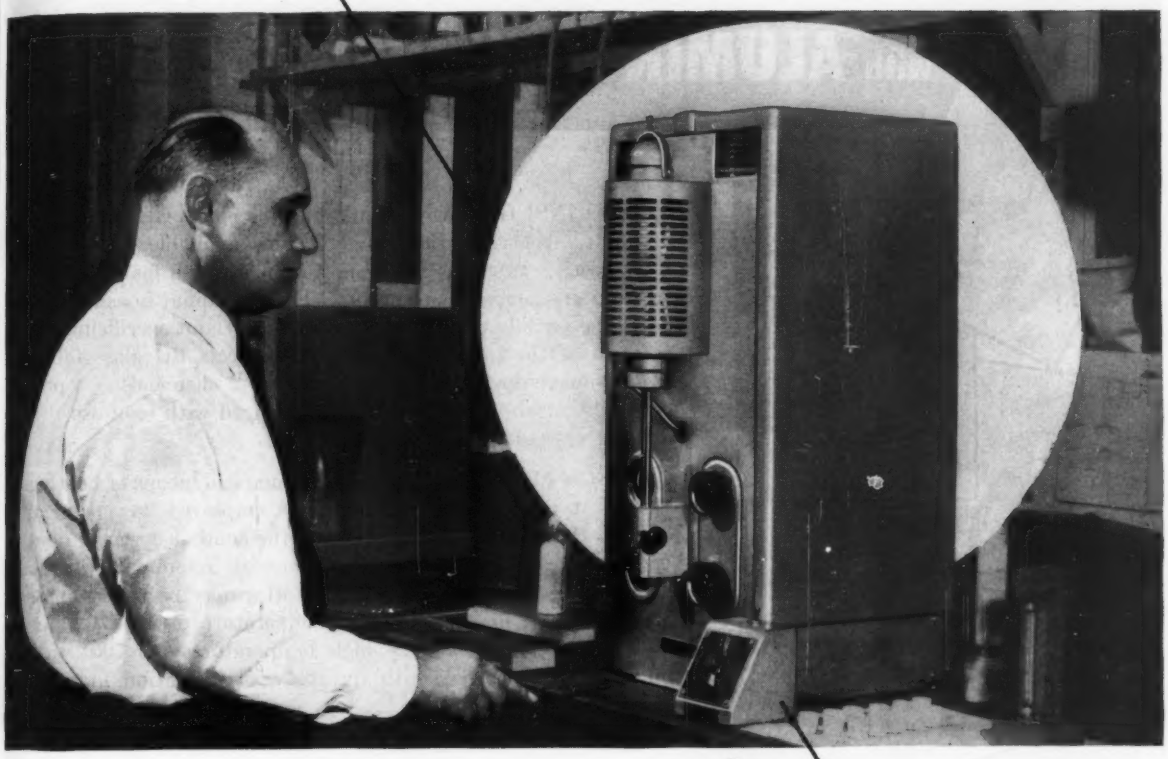

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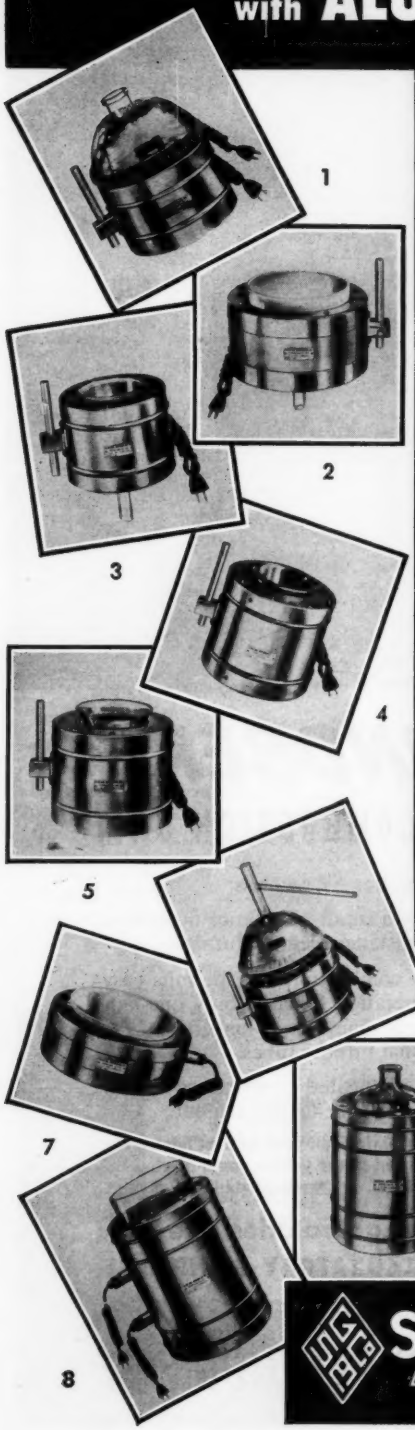

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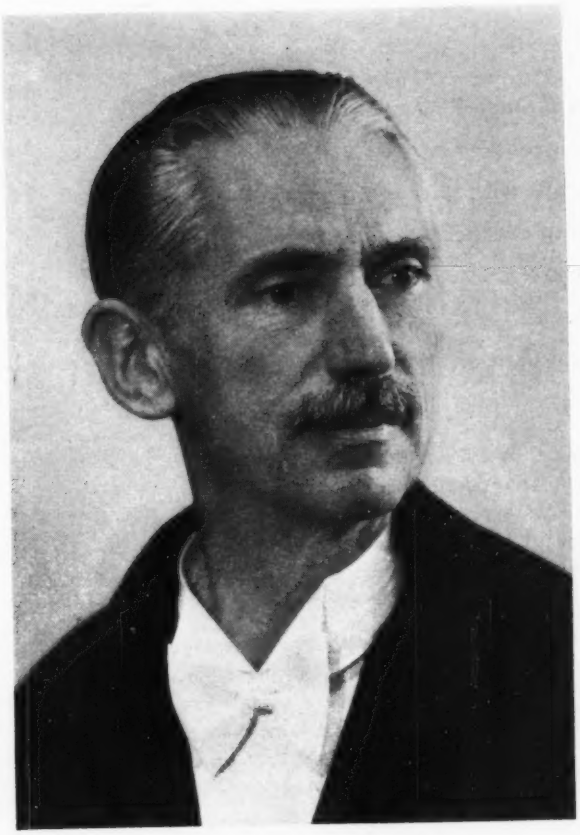

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(see page 622)

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Editor's Outlook

OLDER members of the Division of Chemical Education of the American Chemical Society will remember that the founding of the Division in 1923 grew out of the study and consideration of the problem of correlating the teaching of chemistry in secondary school and college. One of the first, and for many years the most active, committees of the Division was the Committee on Correlation of High-school and College Chemistry. Much of the time was taken up in the early meetings of the Division in discussion of this problem. The early volumes of THIS JOURNAL contain many contributions on this subject.

Then for some time the discussion seemed to have burned itself out. There just wasn't much to be said about it which hadn't already been said many times. The old Correlation Committee was discharged, after several years of activity and the publication of several reports which were carefully considered but which never led to any very tangible results.

For this wasn't—and isn't—a "problem" which can be studied and "solved": it has to be *promoted*. For it is of course a continual situation. And now we find active interest in it building up again. It is proposed to make it a special topic for discussion again at the next meeting of the Division, as well as for one of the Workshops in Chemical Education next summer.

It may be too much to expect anything particularly new but it is true that the situation is now rather different in both college and secondary school from that a couple of decades ago when the matter was under more active discussion. There are recent new movements in professional training and education in colleges which may make new demands upon a student's previous preparation; on the other hand, there is a strong new movement toward "general education" in many colleges, which may have exactly opposite implications. A reconciliation may be necessary between movements in these two directions, which can raise questions for the secondary school.

In the secondary school the whole picture of science education is taking a different form. In many quarters the whole curriculum is being arranged around different centers. It is a real question whether the old conventional sciences will long maintain their identity there. The answer to this is of profound importance to the organization of all science education in the higher institutions.

Like the question of world political ascendancy, these are questions which are now in flux and undecided. But unless we keep them actively before us and participate in the present movements by discussion and persuasion, we may some day wake up to discover that forces outside our control have decided issues for us which we ought to have decided for ourselves.

A STUDY IN SCIENTIFIC GENIUS[1]

Wilhelm Ostwald's Hundredth Anniversary

EDUARD FARBER
Washington, D. C.

THE great expansion of scientific activities in the last few decades has brought with it a definite lessening of appreciation of scientific genius. This result is strange. The opposite might have been expected, but it is generally true that genius has become suspect and is believed to be unnecessary. Recent developments in patent laws may serve as an example for the lowered esteem of genius. A few years ago, the decision in a higher court stated that an invention, to be patentable, should show the "flash of genius." A loud protest resulted from this decision. The protest was so strong that the new, revised patent laws "no longer emphasize the necessity for the 'flash of genius' for establishing patentability, but acknowledge that patentable processes and products may be developed by long cooperative research and development."[2]

Among the many factors which have produced this new trend are the need for more and more tools in research, the multiplication in objects of study, and the longer average life span compared with the times when genius was valued more highly. It is not my purpose here to discuss these factors, but it may be appropriate to state that I believe the trend should be intelligently opposed, in the interest of science and individuality.

When we undertake a study of scientific genius, we have the same attitude as the astronomer toward the object of his study. Knowing the distance and the greatness of our subject, we do not claim its characteristics for ourselves.

We cannot start the study with a definition of its object beyond that which is vaguely, yet recognizably known; its precise definition is the thing to be determined. The purposes of this particular study, however, can be stated in the beginning; they are, first, to describe the functioning of scientific genius by reference to Wilhelm Ostwald and a few other outstanding chemists and second, in doing this, to stimulate our teaching.

Although we know little about human genius except that it is born, we are not entirely helpless in preparing its acceptance and its way. In both directions we can help by education. In studying scientific genius, if only by the descriptive method and excluding attempts at learning more about its genetic conditions, we gain new viewpoints for evaluating our system of education. While this system does not aim at converting every student into a genius, it certainly has the goal of teaching the genius of science and of sparking scientific genius wherever it may lie dormant.

In our efforts to relate or to teach the history of science, we have the task of reintroducing the personal element which is left out of the report about science. This personal element is of really vital importance for the history of science, but we usually cannot do full justice to it. When we present the life story of a great chemist of the past, we often have to do it as if it consisted only of chemical experiment and thought, perhaps with a little play and travel for relaxation. We rarely mention the real struggle with honest competition and all-too-human jealousy. We could be more realistic if we were to discard a reluctance to delve into the personal relations of our chemical heroes. Little use has been made of abundant source material. Where autobiographies and letters disclose personal problems and professional difficulties we need not hesitate to discuss them publicly.

TYPES OF GENIUS

The objection might here be raised that unless we know definitely what scientific genius is, we cannot do anything to further it. To this objection we find an at least partial answer in the history of chemistry. There we always see that successful approaches to the unknown divide it into parts. Before we knew what electricity was, we divided it into a positive and a negative part. Before Macquer (1718–84) or Guyton de Morveau (1737–1816) knew what affinity was, they divided it into classes.

Thus we can start with the division which Wilhelm Ostwald attempted to establish for scientific genius. In making these divisions, no moral or emotional evaluation is implied. According to Ostwald, there are two groups of scientists: the classic type and the romantic. The first are slow and deep-digging, producing their work with long deliberation; the others are swift, brilliant, producing abundantly. As usual in

EDITOR'S NOTE: This is the centenary of Ostwald's birth, 1853. His life and works have been adequately discussed elsewhere. See WALL, FLORENCE E., THIS JOURNAL, **25**, 2 (1948), and BANCROFT, W. D., *ibid.*, **10**, 539, 609 (1933).

[1] Presented before the 124th Meeting of the Division of the History of Chemistry, American Chemical Society, Chicago, September 8, 1953.

[2] *Chemist*, **30**, 359 (1953).

such generalizations, the words themselves needed to be defined once the feeling for what they indicated had been replaced by the question of what they "really" meant. The romantic type thus became the man who created his work out of emotional energies at an early age, and the classic was defined as developing slowly out of a tradition which he carried, in measured step, to new consequences. The source of creative energy and the speed of reaction were the foundation of this division. Compromises and abstractions from personal complexities were needed when such a simple classification was to be applied. Application to real persons was often doubtful, but more important than detailed accuracy was Ostwald's triumphant feeling that a new dualism had been discovered, a feeling which is just as elating, at certain times, as the discovery of a monistic unity is at others.

Ostwald's division of great men into classics and romantics must be taken with a sense of humor mixed with a little awe and some incredulity; otherwise it will become nonsensical. Many authors of now classical fame had the characteristics of romanticism. Certainly the division was not meant to be definite or exhaustive. Ostwald himself also divided scientists into organizers and discoverers. Although he gave equal rank to classics and romantics, he valued the organizer more highly than the discoverer. ". . . The organizer builds at the crossroads, the scientist tends his garden. The first has to be with people because he wants to influence them; therefore, he has to take upon himself all the inconveniences which are connected with congregations of people . . . . In short, he has to submit to the noise, dust, and bad odor which is inseparable from the street . . . . An organizer in science must also be a discoverer, because otherwise he would not have the judgment for that which he is to organize. The reverse is not necessarily true, because a great many discoverers lack the ability to organize."[3]

For Ostwald, the organizer was greater because he must be also a discoverer; he omitted any distinction within the two groups. When he met van't Hoff in 1890, Ostwald recognized him as the greater thinker, while van't Hoff appreciated his friend as the greater organizer and teacher.[4]

One dualism is not sufficient to describe the complex reality of scientific genius, and even with the second dualism Ostwald left much to be desired. I suggest that at least an additional distinction be made between initiators and completers. Here again specific definitions are needed for the generally understandable expressions. Initiators are those scientists who start out in new directions without the ability to reach the fulfillment of their dreams. Completers absorb the energy provided by the new impulse and convert it into a finished structure.

An analogy with the other classification is easy to conceive. The initiators would be closely related to the romantic type, the completers to the classic type.

Other pairs of opposites can be found and correlated with each other. For example, the distinctions between experimenters and theorizers, teachers and writers, scientists and industrialists, are easily recognized as having the same validity as the ones mentioned before.

In addition, we could establish "types" which have no complementary counterpart: the egocentric genius like Paracelsus, Liebig, or Berthelot; the visionary genius of Kekulé, Mendeleev, and Alfred Werner; precisionists such as Cavendish and Otto Wallach; unitarians like Berthollet, and dualists like Berzelius. However, in every one of these types we can find the characteristics of others. Ostwald himself might be compared to Paracelsus, Liebig, Kekulé, or Berthollet in certain phases of his work.

Such resemblances in parts simply mean that the complexities of scientific genius, or of any other individuality, are only primitively captured by establishing such groups as classicists and romanticists, discoverers and organizers. At best, they are as close to the truth as were the four Aristotelian elements compared with the 98 chemical elements and their hundreds of isotopes.

DUALISM AND MONISM

The separation of scientists into two, or two pairs, of groups is perhaps the only dualism in which Ostwald believed. In all his other thought and work he was governed by monistic concepts long before he turned to the philosophical system of monism, about 1910.

When dualism is considered as the opposite of monism, the problem is whether both have equal rank. A secondary dualistic division, like that of energy into potential and kinetic, would not invalidate the monism in the concept of energy as Ostwald proclaimed it. However, in the course of Ostwald's life we can recognize a primary dualism.

When he was 21 years old, he studied Julius Thomsen's work on thermochemistry. "Like lightning, the thought occurred to me that instead of heat development, every other measured quality of the solution could serve, provided the quality is sufficiently influenced by a chemical change."[5] Thereupon he selected specific gravity as one "other quality" and felt he had inaugurated a new system of chemical research, "volume-chemical studies." He viewed his experiments as part of a complete entity, and therein lay his monistic attitude.

This relationship between rational effort and insight recurred in several decisive moments of his life. In the spring of 1890 he experienced, in a sudden illumination, with "an almost physical sensation in my brain," the great conception of energy. To be capable of such deep experiences, to be subjected to them, to embrace them as immediately compelling and revealing is a common trait of scientific genius. Ostwald compared his inspiration of that spring day with Robert Mayer's experience, just fifty years before, in which he dis-

[3] OSTWALD, WILHELM, "Lebenslinien, eine Selbstbiographie," Klasing & Co., Berlin, 1933, part III, p. 435.

[4] *Ibid.*, part II, p. 130.

[5] *Ibid.*, part I, p. 117.

covered the law of conservation of energy. Did he discover it actively, or was he overwhelmed by it? At the moment of such an *Urerlebnis*, a primordial experience, a human genius meets in greatest freedom the idea which is to govern him. For Proust, it was an analytical figure revealing the same composition of natural and of artificial copper carbonate. For Amé Pictet (1857–1932), it was the sight of the diagram of a pyridine ring seen in the window display of a book. Such primordial, inspiring experience speaks only to one person, only to him it is more than a single fact. Most of the events of our common experience dimly impress upon us complexity and vagueness; they belong to rule and habit or to meaningless accident. Then, suddenly, our experience glows with importance and radiates meaning. Often a lifetime is required to explore and express this meaning.

Ostwald would not have agreed with this emphasis on the importance of subconscious, therefore almost mystical, influences on the life of scientific genius. He did not want to be considered a genius. When he described the development of his system of measuring color, he added: "I do not doubt, for example, that Helmholtz would have created the measurement of color if he had been as conversant with paints and brushes as with partial differential equations."[6] Clear thinking based on practical experimenting is all that went into "the greatest achievement which it has been given me to perform."[7] In his "Malerbriefe" (letters to painters), 1904, he wrote: "The artist shall create consciously," that is to say, rationally, selecting his colors according to the rules of harmony which Ostwald had established. There should be no dualism between art and science.

A discussion of dualism and monism in science could use many examples from the development of chemistry. More pertinent to the present topic is an event in Ostwald's life which illuminated the complexities of such a discussion. In 1895 he gave a public lecture on the advance over scientific materialism for which he almost received an honorary doctor's degree in theology. Actually the materialism against which he spoke was not so much the opposite of idealism; it was atomism as opposed to energetics. And a few months later Roentgen's discovery led to the scientific proof of atomism which Ostwald soon admitted.

ENERGY AND CATALYSIS

In a broad sense, catalysis is the dualistic complement of energetics. Robert Mayer, with whom Ostwald had once compared himself, discovered foundations of both concepts, energetics in his law of conservation, catalysis in his study of release ("Auslösung"). He felt that the great and ancient law that cause equals effect needed modification. In 1845 Mayer simply stated: "A force is called catalytic insofar as it has no relationship in magnitude with the contemplated effect." Thirty years later, in his last publication, he explained: "Very many natural processes take place only when they are initiated by an impact, and it is this occurrence which modern science calls release." When released, the forces are governed by the laws of energetics, but the release itself is outside those quantitative relationships. Ostwald naturally could not accept Mayer's first statement; catalysis could not be a "force." In the definition of 1890 it was a process produced or accelerated through the presence of certain substances. The first alternative was omitted in the definition of 1894, so that catalysis now exclusively belonged to the field of kinetics.

Ostwald considered the conceptional definition of catalysis his most original chemical work with the greatest consequences.[8] He made objective what he had personally experienced of the releasing, or catalytic, force of sudden inspirational insights. They opened his eyes to the universal importance of energy, which he then saw as the constancy or invariance of a self-identical substance. "A metaphysical interpretation is implied which exceeds the mere content of the physical principle."[9] From the historical-critical point of view, Ostwald's introduction of such a metaphysical concept resembles the introduction of the atom in the connotation which he so strongly rejected.

THE LAW OF INGRATITUDE

In the introduction to his book on Rembrandt, Carl Neumann speaks of "an apparent historical law of ingratitude which separates the generations from each other." In the lives of outstanding scientists and inventors we sometimes find that they were dissatisfied with the reception of their work. A law of ingratitude could easily be constructed in summarizing the experiences of teachers with their students, of professors with their assistants, of creative men with the public which benefited from their work. Ostwald's autobiography frequently mentions envy and jealousy of colleagues, "a decided personal aversion against me."[10] Yet he became professor at the University of Leipzig at the age of 34. A new institute was built for him ten years later. He had scarcely resigned from his professorship in 1905 when he became the first exchange professor, upon invitation by Harvard. He received the Nobel prize in chemistry for 1909. These signs of gratitude came from large scientific bodies, but regarding single persons he felt that he lacked "the art of dealing with people."[11]

In our emphasis on cooperative work we often stress as requisite the ability to lead and to get along with people. When we consider the characteristics of scientific genius, we may incline toward a reversal and stress the need for people to get along with genius—provided we value genius highly enough. The reasons for Ostwald's complaints are easily understood.

[6] *Ibid.*, part III, p. 19.
[7] *Ibid.*, part I, p. 30.
[8] *Ibid.*, part III, p. 196.
[9] SCHLICK, MORITZ, "Philosophy of Nature," The Philosophical Library, New York, 1949, p. 113.
[10] OSTWALD, *op. cit.*, part III, p. 307.
[11] *Ibid.*, part II, p. 104.

"Normal" people will talk about their problems with friends who may have experienced similar situations; Ostwald relied, instead, on such communication from books or on analogies with biological-physical rules. After returning from a semester's vacation, in the fall of 1896, "the former unlimited pleasure in scientific handiwork was gone."[12] He found consolation in remembering that he had read an article on the "forty-year sickness." To the usual and mutual support of friends he preferred the recognition of general laws, superior forces which guided his life and which he proclaimed as the laws of all life. No wonder that his friendships were few, that he encountered what he calls envy; perhaps it was only unwillingness to accept him in the role of lawgiver or, to say it more simply, as the man who knows better. But while he was not a good mixer, his need for support by impersonal forces gave us the great number of his efforts in the history of chemistry. He inaugurated the *Klassiker der Naturwissenschaften* in 1888, completed a history of electrochemistry in 1895, and presented the principles of chemistry in many forms, always including its history. For his great "Lehrbuch" (1884) he selected "the historical-critical form," and in the second edition (1890) he again emphasized the value of history: "I have continually endeavored to present clearly the historical development of the several fields of science, and I hope thereby to contribute my part to the revival of an historical sense in scientists which still is in need of being developed with great care." However, to him history was valuable only as a method and tool, not as a science.

His answer to ingratitude was more work for the improvement of education and for the organization of scientific work. His answer to praise of his work was equally proud. In his Nobel Prize lecture he congratulated the members of the Nobel Institute on their good judgment in selecting the really best part of his chemical work for the reward. Such a statement could sound presumptuous when made by a "normal" person; but Ostwald was not a normal person; he did not speak of himself except as he identified himself with the system of science in which he was absorbed to the extinction (and, paradoxically, glorification) of his individuality.

BETWEEN NATURE AND SOCIETY

We have followed Wilhelm Ostwald's path through science as he observed it, and we have compared it with other life stories. We have seen a scientific genius at work in science and its organization, and we have seen the philosophical problem of the individual versus the community experienced in a conscious, emotional life. The problem was not solved thereby; it was only stated and verified. We would have been too much persuaded by our hero if we had accepted his view as the generally valid one. Modesty and arrogance are strangely intermingled in his view, the modesty that of feeling himself just one of the realizations of a general law, and the arrogance that of having found this law in all its generality. His own attitude would justify us if we were to state that he was the model of scientific genius *per se*, or at least of the one class of two which he felt himself to exemplify. The evidence of history shows that we cannot do this. Individual scientists are too singular; they do not repeat a recognizable pattern. Yet we can describe certain common traits and try to approach, though incompletely, the definition which we sought in the beginning.

Scientific genius is characterized by the ability to note the common features of special observations, the links between special facts. We call these laws of nature, as if nature were a jurisdictional entity presiding and watching over the behavior of things and organisms. Do we really mean this by "law of nature"? No, it is just one of the great number of designations not to be taken as adequately descriptive of what we mean. We should have changed this particular designation long ago, at least since the time when Kant carefully demonstrated that it is not nature but *we* who prescribe these laws. Philosophers then went on to explain that we are able to find and formulate these laws because we ourselves are nature's instruments. Scientific genius is related to the mystic in bringing nature to our consciousness, in revealing its "secrets." If this sounds too metaphysical it indicates that we have to overcome an aversion against metaphysics when we try to study scientific genius.

The strength of the conviction that he speaks for nature gives the genius the courage to persist in his teaching even against the resistance of the experts. Proof through experimental results is never complete and therefore always open to objection. On the other hand, scientific revelation through inspired unity with nature is confined to the experience of one man. Later on, it is objectively connected with general experience which is verified in practical application. Again, the courage to persist is important. Existing practical application may be at fault while opponents charge the genius to be in the wrong. And here we arrive at the practical application of the results obtained in our apparently theoretical study of scientific genius. It is not enough to rely on nature to select its spokesmen and to give them the courage of their vision. We have to participate in nature's work through education.

This courage to persist is founded on inner conviction, on a communication with nature which carries with it the urge to let society participate in the result. Schoenbein, in many respects the southern predecessor of Ostwald, once wrote to his friend Liebig (March 14, 1854): "Without the courage to express a new thought, even at the risk of erring or of being called a fool, a man will contribute little to any kind of progress."

Courage, although the sign of expressed individuality, can be understood as the reliance upon a super-individual force derived either from nature or from society. Scientific genius derives this force from nature, political genius from society. However, the two are not absolutely separated; they are connected by

[12] *Ibid.*, part II, p. 223.

tension like that between potential and kinetic energy. The dualistic tensions are, perhaps, of fundamental importance in understanding scientific genius. Opposite attitudes, like those which Ostwald ascribed to basically separate types of great men, are present in one individuality and cause the tension which genius translates into production. "It is important to consider that the struggle between classicism and romanticism also exists within every mind. And it is from this struggle that the work is born." André Gide said this in speaking of the artist, but it is true also of scientific genius.

HOW I CAME TO KNOW WILHELM OSTWALD

EBERHARD BRAUER
Ostwald Archiv, Haus Energie, Grossbothen, Saxony
(*Translated by Ralph E. Oesper*)

When I was a pupil in the third district school in Leipzig, my teacher urged me to enter the nearby Realgymnasium. So, after a short period of preparation by a theology student who was boarding at our house, I entered the fourth form on trial—and found myself faced with two entirely new problems. One was the inadequacy of my preparation in Latin, which I had studied under a private tutor. The other was the attitude of my newly acquired school-fellows. At the first marking period my grade in Latin was a poor 4, but at the second report I received a 2*a*, and the third mark was an excellent 1. To most of my fellow students I long remained an outsider, but not to the one who accompanied me on the last part of the way to school.

There was a good reason for this. He profited from my translations and from my aid in mathematics, and also from the toys which I had made, such as a boat with a rubber-band motor which was tried out in the bathtub of his foster-parents. Another time it was a batch of homemade gunpowder, which he tried out at the wrong time and place. His justifiably alarmed aunts and foster-mother called me in and thus I, for the first time, entered the home which was to have such a dominant part in my future scientific and personal life. The feminine storm soon blew over and was replaced by a warm interest in my particular lot, and from time to time I was a guest in the Ostwald household.

However, I seldom saw Professor Ostwald there. The few times were so impressed on the memory of the young boy, that I still remember clearly all the details of these eventful encounters. For example, on one occasion, he examined the photographic apparatus I had made. I still see him standing before me, his upright figure, his eyes that often were directed into the far distance, his rapid gait, the contrast of his reddish beard and the blue of his eyes, the fresh color of his skin, the thick hair combed straight back.

After my school friend had gone back to Riga, my friendship was transferred to the two older Ostwald boys, Wolfgang[1] (1883–1943) and Walter. Wolfgang's tastes ran to zoology and music. I was a willing listener to his improvised rambles in the world of music. But I also was the older comrade to these fine boys in the more intimate confines of this German home. With Walter I shared an intense interest in everything driven by a motor, and the yearly automobile shows in the Leipzig Kristallpalast fascinated both of us.

Consequently, it was almost a matter of course that, after graduation from the secondary school, I would go to study chemistry with Professor Ostwald—especially since he relieved my financial troubles with a stipend.

In the beginning I worked in the analytical division with Professor Julius Wagner. Here I not only learned laboratory methods as such, but I also occasionally helped out some of the older students with their dissertation labors—assistance which gained me many friends.

Wilhelm Ostwald had included a student workshop in his new Institut on the Linnéstrasse. While I was still a student in the lower school I had constructed a simple master lock for the large demonstration table of the Realgymnasium; it proved most valuable and gained the approbation of the two teachers. Consequently, the well equipped shop in the Ostwald Institut was most welcome to me, particularly since Wilhelm Ostwald set us all an example by working there himself.

Each year, the Christmas season was inaugurated in

[1] Oesper, R. E., this Journal, 22, 263 (1945).

the Institut by a large party attended by the Ostwald family, the assistants, and the students.[2]

Professor Ostwald frequently invited foreign personalities to share in these celebrations. The guest gave a lecture on his specialty and then participated in the harmless, good-natured jollification planned by and for the Institut family. The high point of the party was the distribution of the carefully selected humorous gifts. Punch and cakes, prepared by the Ostwald daughters, were another feature of these parties. The younger one, Elsbeth, had attracted my special attention, but it was not until many years later that she became aware of my feelings toward her.

The semesters devoted to laboratory courses passed quickly and smoothly. They also brought many occasions on which I made myself useful to Professor Ostwald. For instance, I arranged his library of reprints, and I also served as assistant in setting up his demonstration experiments, a responsible but not too arduous duty.

At his suggestion, I made some studies of the catalytic synthesis of ammonia from the elements, but the results were not what we had hoped for. In connection with his studies of the periodic phenomena observed in the solution of metallic chromium, I recorded the accompanying electrical behavior as shown by a galvanometer. These findings constituted the basis of my doctoral thesis.

After I obtained my degree, Ostwald asked me to stay on as his private assistant. He entrusted to me the studies of the conversion of ammonia into nitric acid. This research was conducted at first on a small scale in the Institut laboratory. He then made arrangements with Professor Will of the Zentralstelle für wissenschaftlichtechnische Untersuchungen for technical-scale trials. At Christmas, 1901, I moved to Berlin. I had some hesitation about making this move which involved a certain degree of independence. He reassured me by saying, "Just buy yourself a handkerchief and go ahead." I still have this handkerchief.

Within a few weeks, on January 27, 1902, a self-prepared, burned-clay plate with a set-in platinum catalyst, produced nitrous vapors from measured air-ammonia mixtures. However, the matter was not quite so simple; the production of pure nitric acid required several years of uninterrupted labors. The advances and also the setbacks were recounted by Wilhelm Ostwald in the *Festschrift* of the platinum firm, G. Siebert, under the title "Platin als weltgeschichtlicher Factor."

Thinking back to that period when I was working on the catalytic production of nitric acid and when, as Wilhelm Ostwald's assistant, I was attempting to translate his ideas and suggestions into technical practice, I realize that our personal relationships grew increasingly more intimate, and that his interest in me was not only friendly but bordered on the paternal. Whenever he visited me, he not only discussed the problems connected with our researches but brought up matters of more personal interest. For instance, he helped me to acquire for my parents a little orchard plot and cottage, insuring them a pleasant home in which to spend their old age.

Wilhelm Ostwald (at the time of his appointment to the chair of physical chemistry at the University of Leipzig)

My bonds with the rest of the Ostwald family also continued most cordial and friendly. The second son, Walter, shared my bachelor quarters for several months while he was working on the development of a slag gasification process. When, on the other hand, I visited the Ostwald estate at Grossbothen, I could always count on a warm welcome from the Frau Geheimrat, even though she was certainly aware of my poorly concealed interest in her daughter Elsbeth. It was a long time before I dared declare myself formally as a suitor, but one day I received an encouraging telegram from Frau Ostwald and I then felt free to seek the consent of the young lady of my choice.

It was an auspicious star that lighted the way which led the young schoolboy into the Ostwald home, which allowed him to participate in the great master's works as assistant and collaborator, and which finally gave him many years of personal happiness as his son-in-law.

[2] For an account of these Christmas festivities see FOULK, C. W., *ibid.*, **11**, 355 (1934).

HOW ONE BECOMES A CHEMIST[1]

WILHELM OSTWALD
(Translated by Ralph E. Oesper)

As you well know it has long been the custom in our laboratory each year to celebrate the advent of the Christmas season together. These enjoyable gatherings began in our old Institut on the Brüderstrasse, though admittedly the outer forms have now been somewhat changed. It began in a very modest way; we sat on the tables and watched the *Diener* ceremoniously deliver to each a humorous present, and of course I too received a well considered gift of the same kind. During the pauses we divided our attention between punch and spice cakes.[2]

A change was made when we moved into our present quarters. Now we use tablecloths, the room is decorated, and the whole atmosphere is more festive than formerly. The most striking new feature, however, is that each year an eminent chemist is present and he has to pay for his participation by giving a talk. Thus we have been honored by Landolt, Ramsay, van't Hoff, and other great men of our science, and each of them has had to report on his researches, so that we have not only seen but heard these leaders. Unfortunately, this year we are not to have this pleasure. I intended to share my friend Arrhenius with you this year, but he has had to cut short his present stay in Germany. Our science is not very richly endowed with great personages and so I could not find a replacement in time. Therefore, it is necessary for me to step into the breach, though by doing so I am not presuming to put myself on the same plane as the others. I wish to tell you a story and I have chosen it because of something that is occupying my thoughts at present, namely, this question: how does one become a chemist? I regret that my thoughts on this subject have not yet developed to the point at which I could present them to you in a well-systematized form, and so it will perhaps be better if I relate to you how it came about that I became a chemist, and I will then leave it to you to extract from my talk what you may consider essential.

When I carry my memories back as far as I still can, I see myself sitting on some steps leading to a wharf. I had a fishing rod in my hand and I was busy trying to catch some of the leeches that abounded in the canal below. This attempt to catch leeches is connected in my memory with the first scientific experiment that I remember making. While I sat there, waiting for a bite, one of my father's friends (my father was a cooper) came out of the house and gravely warned me to beware of the leeches, lest the first one to bite would pull me into the water. At first I was quite frightened at this prospect, but I soon got control of myself and reasoned that if the leech should try to pull me in, I could simply let go of the rod. On this basis, I continued my fishing, but unfortunately the experiment led to no satisfactory result because none of the leeches was inclined to take hold of the hook.

This canal and its surroundings served in the succeeding years as the scene of my gradually increasing activity as a researcher. Along with my brothers—one older, one younger—and several friends, I thoroughly explored the contents of the canal, and every new find was discussed extensively by the whole group. This activity gave us a great deal of pleasure, though my mother's enjoyment was somewhat less because our discoveries created all sorts of disturbances in the household.

This sort of thing went on for a while until one day I got my hands on an old book which contained detailed directions for making fireworks. I immediately became interested and enthusiastically set to work to find out if I could make the beautiful colored fires described in the book. The first trials worked rather well and although my friends and I did not have much choice of materials to draw on we eventually got together the most necessary ingredients and from then on we devoted ourselves to pyrotechnology by land and by water. The success of these efforts finally emboldened us to consider seriously the possibility of our making a real rocket. After some hesitation, we made the attempt and at last the rocket was finished. It now had to be tried out. After some discussion we decided that we would set off the rocket in the flue of the kitchen chimney, where it could do no damage. Actually we were convinced that this was a superfluous precaution because none of us dreamed that the thing would really go off. To our amazement, however, the rocket shot directly into the chimney; I do not know whether it came out the top or not. This result encouraged us to start the manufacture of fireworks almost on a factory scale, again to the distress of my mother, whose pots and pans often found uses that were not anticipated when they were purchased.

My interest in chemistry developed as a sequel to these experiences with fireworks. This same book contained an introductory section acquainting the pyrotechnician with the most important chemical questions touching his field. I faithfully studied this text and

[1] This was a Christmas talk delivered in the Physikalisch-Chemisches Institut of the University of Leipzig on December 19, 1905. The stenographic notes by Dr. Carl Drucker (now of the University of Upsala) were kindly placed at the translator's disposal by Miss Grete Ostwald of the Ostwald Archiv, Grossbothen, Saxony.

[2] See Foulk, C. W., this Journal, **11**, 355 (1934).

so laid the foundation of my chemical training. I also learned to prepare some of the materials that I needed, and in addition gained some facility in learning to help myself when the book failed me.

About the time I left elementary school and entered the Realgymnasium, I became interested in another field; I began to take pictures. Photography was not so simple then as it is now. Today you simply buy dry plates and snap the picture. At the time I am speaking about, each plate had to be poured by the photographer himself; the solutions had to be properly compounded, and when the plate was finished there was no certainty that the exposure and subsequent development would result in a picture. In such difficulties I found it useful to apply a principle which I earnestly recommend to you as a guiding principle. Whenever you wish to do something but have little hope of success, you will find that the best aid is to brag loudly that you are going to accomplish this feat in a certain time. You thus publicly commit yourself to work on the job regularly and continuously, whereas you otherwise would be very likely to get fed up with the task, and every morning have to struggle with yourself to tackle it anew—a struggle which, as you well know, increases markedly as time goes on. I made use of this moral principle on the occasion I am referring to now and induced a friend—I purposely chose the best looking one—to bet that I could not deliver a good picture of him at a set time. I devoted all my efforts to the task and actually delivered the photograph on time. The subject claimed that he had not been posed to the best advantage, but in the opinion of the arbitrator he was no better looking than the photographic likeness, so I won the wager.

My progress in school was not favorably affected by these distractions. As I told you a little while ago, I was now enrolled in the Realgymnasium, and this was in fact one of the most ideal schools of which I have ever heard. You will see why in a moment. I had only five years, but because of my extracurricular interests, which interfered seriously with regular studying, I made seven out of the five years. Another handicap was the difficulty I always had with the appalling Russian language. This also plagued me considerably at the time of my final examination. In fact I overcame this hurdle only because of the understanding help of my instructor, Popen. Translation exercises had to be written out under his guidance before the examination, and by a singular coincidence, the very last of these exercises was precisely the one that appeared in the examination. In short, I managed to get through and was ready to enter the university. Accordingly, the great day arrived for me to leave Riga and begin my student years at Dorpat.

The conditions at Dorpat were unusually alcoholic. I joined an association of students from my own country, as was then the custom, and through this fraternity was led to cooperate in the consumption of enormous volumes of beer. This activity took up a large fraction of my time, especially during my first two semesters, but I made up at least a part of this loss by regularly not attending classes and lectures, since in those days listening to lectures had a pronounced soporific effect on me.

When, some time later, I was permitted to begin laboratory work in chemistry, I began with qualitative analysis under the guidance of Johann Lemberg, who died not long ago. At that time he was still a rather young man and had really queer habits. For example, he never used a salt cellar, but instead kept a paper bag on the table, which he replaced when necessary with another of the same kind. The students of that period retain vivid recollections of Lemberg's overcoat. When I first came to know him, it was just turning from green to blue. Later it became brown, which reportedly had been its original color. Although he published but little during his lifetime, you can get an idea of his scientific competence from the fact that he had clearly worked out the law of mass action long before Guldberg and Waage and had consciously applied it to geological problems.

The first semesters passed quickly in the manner I have described. I played viola in quartets a good deal and took part in other kinds of distractions. We were constantly playing jokes on each other and having a good time in general. Nonetheless, after several semesters I applied for permission to take the first part of the candidate examination—it was normally taken in three parts. Contrary to expectation, I made a good showing. This success so emboldened me that at the celebration in honor of my triumph, attended of course by the others who had likewise come through the ordeal in good fashion, I suddenly announced that I was going to take the second part at the next opportunity. This was looked upon as unabashed bragging on my part, because the examination was only a couple of weeks away. The ridicule that followed irritated me to such an extent that again I took refuge in the moral imperative and wagered a basket of champagne on the outcome. The next morning things did not look so rosy as they had the night before, and I was inclined to shrug off the whole idea, but then I remembered the wager and this made me give the matter serious thought. I decided that it would not be entirely silly to at least attempt the examination. In short, the experiment succeeded, but naturally I never saw the basket of champagne. However, I was appointed assistant to Professor von Oettingen in the physics laboratory. There had been another candidate for the post, and von Oettingen would really have preferred him, but he had only taken the first part of the examination. The professor later told me that he certainly did not anticipate much benefit from me at the time I was imposed on him.

The duties of my post were not very arduous, since there were but few students to look after. In addition, I had only to help in setting up the apparatus. Consequently, I had much free time and von Oettingen advised me to use it for independent research. "Never again in your whole lifetime will you have a similar,

quiet, undisturbed period for your own work." How right he was! I began a problem with much enthusiasm but there were times when I discontinued work for long stretches. I remember particularly one day in the middle of the spring. It was wonderfully warm outside and a lilac bush in full bloom wafted heady perfume into the open window of the balance room where I sat weighing out acids. The contrast between the odor of the lilacs and the smell of the butyric acid was too much for me; I got up, left everything as it was, and did not return for eight days.

We had a small private orchestra that was directed by von Oettingen. Unfortunately, one important instrument was not represented, namely, the bassoon. Since a bassoonist was essential, one of us had to sacrifice himself and as the professor's assistant there was little choice for me except to learn to blow the bassoon. Accordingly, I began with the usual beginner's exercises, which I practiced in my room in the laboratory. Karl Schmidt, who had the room just below mine, later told me with what interest he had followed my progress and how great was his joy at the growing recognizability of certain notes. I must have made definite strides forward, even though on orchestra nights Professor von Oettingen still invariably said, "My dear Ostwald, will you be good enough to take the viola?"

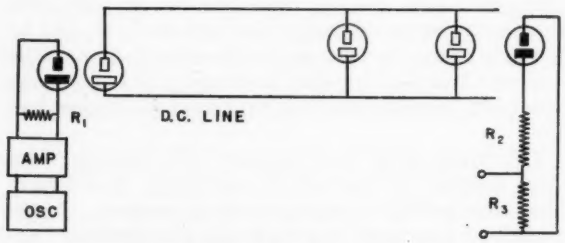
In due time I passed the master's examination and thus acquired the privilege of giving lectures. This period of my development was also marked by an event whose results I am still enjoying, namely, my engagement and marriage. After I became engaged, one of my close friends warned me in all sincerity against going ahead with this venture, arguing that I had made an excellent start in science but now would never accomplish anything worth while, which would really be a shame for me and the world in general. However, his arguments fell on deaf ears.

One year later I passed the final examination, the doctoral, and became a professor. I think it is hardly necessary to subject you to a recital of my subsequent career, since I am sure that most of you have at least some knowledge of the contents of these many years. Besides, it is at last time for our Christmas celebration.

A 1000-CYCLE DISTRIBUTION SYSTEM

ALEXANDER P. MARION
Queens College, Flushing, New York

For several years the following scheme has been used to distribute a 1000-cycle voltage throughout the elementary physical chemistry laboratory with negligible interaction and no observable distortion of the wave form. The wiring normally used to carry direct current to the laboratory tables is isolated from the generator by pulling fuses and the output of a 10-watt amplifier driven by a 1000-cycle oscillator is plugged into a d.-c. outlet at one of the tables. The highest impedance of the output transformer is selected and loaded with an equivalent amount of resistance. In this installation, for example, the 500-ohm terminals of the output transformer are used and are shunted by a 500-ohm, 10-watt bleeder resistor. Under load about 30 volts are delivered to the line.



R_1 = 500 ohms, 10 watts
R_2 = R_3 = 75,000 ohms, 1 watt

Two 75,000-ohm resistors are mounted in series on a small board and can be connected to the 1000-cycle line by means of ordinary POSJ lampcord and a polarized plug. (Use of a polarized plug prevents accidental insertion into an a.-c. receptacle.) Fahnestock clips are mounted on the board at each end of one of the resistors and serve as the student's source of the 1000-cycle signal.

Measurements of resistances ranging from 60 to 30,000 ohms by the Wheatstone bridge method have been satisfactorily performed by eight groups simultaneously. Even should a short circuit develop across one station there is a change of approximately 0.5 per cent in the supply voltage and this ordinarily is not detectable.

THE VACUUM FUSION METHOD FOR DETERMINING MINUTE QUANTITIES OF GASES IN METALS

WILLIAM J. McMAHON and LAURENCE S. FOSTER
Watertown Arsenal Laboratory, Watertown, Massachusetts

THE use of conventional analytical methods to determine very minute amounts of gases which are ordinarily present in metals is a tedious and inaccurate procedure. Gaseous impurities, particularly oxygen, nitrogen, and hydrogen, are present in very small amounts in all metals, and further minute quantities may later be acquired through adsorption or absorption by the metal as a consequence of its use. The presence of such gases even in extremely small quantities may produce marked effects on the chemical, physical, and mechanical properties of the metals.

Gaseous elements that are responsible for impurity effects may be present as occlusions in the metallic structure, in solid solution, or in chemical combination as precipitated grains of oxides, carbides, or nitrides. Some of the mechanical properties, of particular interest to the metallurgist, which have been found to be significantly affected by gaseous impurities are impact resistance, ductility, and drawing characteristics. Moore and his co-workers (*1*) at National Research Corporation, investigating the strength characteristics of high purity iron at elevated temperatures, were able to demonstrate the adverse effects of individual gaseous impurities. Nitrogen was found to have a significant effect on the strain sensitivity, demonstrated by a marked decrease in impact value after working. An increase in nitrogen content was also accompanied by a decrease in stress-rupture life. For example, at 800°F., the length of time a specimen containing 0.0001 weight per cent nitrogen would withstand a stress of 10,000 pounds was more than 1440 hours; when the nitrogen content was increased to 0.012 weight per cent, the length of time to rupture was reduced to 2.9 hours. A similar decrease in stress-rupture life was noted when the oxygen content of iron was increased up to the solubility limit in the solid (0.008 per cent). After this point had been passed, further addition resulted in a steady increase in stress-rupture life up to the highest oxygen content tested (0.05 per cent). This endurance to stress, however, is still considerably less than that of the high purity iron.

Other investigators have compiled data which further demonstrate the adverse effects on metals of gaseous impurities. Hochmann (*2*) described a significant increase in impact resistance and a downward shift in the temperature of transition from the ductile to the brittle phase of chromium alloys when gaseous impurities were reduced in amount. Stauffer (*3*), investigating the effect of oxygen in copper, reported greatly improved electrical conductivity as a consequence of the reduction in gas content. The conductivity of his high purity copper was better than the international annealed copper standard. A recent paper by Smith (*4*) points out in a fundamental way the role that gaseous elements play in altering the cohesive forces in metals. He experimented primarily with hydrogen. The widening of the crystal lattice which he observed was found to be responsible for at least some of the differences in mechanical, magnetic, electrochemical, and chemical properties.

These specific examples have been included only as illustrations of the effects of gaseous impurities, and should not be construed as a complete survey of the field. Numerous other references are made to the effect of gases in metals in the metallurgical literature.

PRINCIPLES OF VACUUM FUSION

Ordinary analytical techniques are not sufficiently refined to determine gases in metals in the low percentages that prevail. It has been necessary to evolve new techniques. Radioisotopes generally may not be used, since suitable isotopes are usually not available. Mass spectrometric methods, involving use of stable isotopic tracers, might be applied, but only recently have solid sources been made available to attack (*5*). The method most commonly in use today is the vacuum fusion technique.

Apparatus and procedures vary somewhat from one investigator to another, but the chemical principles upon which these methods are based remain the same. The metal specimen is melted in a graphite crucible under vacuum. The oxygen and combined oxides react with the graphite of the crucible to produce carbon monoxide. The nitrides and hydrides are simultaneously decomposed and nitrogen and hydrogen are liberated as the elements. Carbon is somewhat soluble in molten metals and because of this solubility comes into intimate contact with the oxides and nitrides. Typical reactions are:

$$H_2 \text{ (dissolved)} \rightarrow H_2 \text{ (gas)}$$
$$FeO + C \rightarrow Fe + CO$$
$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$
$$2Fe_2N \rightarrow 4Fe + N_2$$

The combined gases are exhausted from the furnace,

collected, and analyzed in the apparatus shown in Figure 1. A photograph of the actual equipment is reproduced in Figure 2. To determine the amount of carbon in a sample, a specimen may be heated similarly in a ceramic crucible under a partial pressure of oxygen. CO is evolved and determined in an identical manner.

APPARATUS

The apparatus consists essentially of a high-temperature furnace, an evacuation system, and an analytical system. The furnace is most conveniently heated by high-frequency induction.

Induction heating is accomplished by subjecting the graphite crucible within the furnace assembly to a rapidly alternating electromagnetic field. This field is imposed within a water-cooled helical coil of copper tubing surrounding the furnace. A high-frequency current is applied to the terminals of this coil and any electrical conductor located within the field has a current induced in it which heats it rapidly to high temperatures. The amount of energy (heat) is proportional to RI^2 watts (ohm-ampere^2). By this means the crucible and metal charge can be heated to the high temperatures required (1600 to 2400°C.) without heating the non-conducting glass furnace shell. Heating of the shell and other furnace components in the vicinity of the melting crucible is minimized by surrounding the crucible with insulating material and radiation shields. McGeary, Stanley, and Yensen (*6*) packed their graphite crucible in graphite powder inside a graphite radiation shield. Induction heating of the shield was prevented by cutting vertical grooves to interrupt the electric circuit. Mallett (*7*) packed his melting crucible in graphite powder in a beryllium oxide thimble that rested on a bed of alumina sand. The graphite melting crucible was then slipped inside the heater crucible and could be discarded after each analysis. Guldner (*8*) of the Bell Telephone Laboratories has developed a furnace that has many attractive design features. An Acheson AGR graphite melting crucible is packed in sub-200 mesh graphite powder inside a quartz crucible about twice its diameter. This assembly is suspended from the top of the furnace guide tube by platinum wires. This type of suspension minimizes the volume of material that must be heated to high temperature. A guide tube, to lead samples into the melting crucible, is provided. The furnace jacket is made of Pyrex glass and is air cooled by means of a blower. Some other furnace designs have provided cooling by a water jacket. This, however, has not proved to be as satisfactory in practice as air cooling, because the more volatile metals show a greater tendency to condense as metallic films on the cooler upper portions of the water-cooled furnace. The presence of such metallic films can cause serious "gettering" effects, contributing to low analytical results by combining with evolved gases. Even where air cooling is used, some condensation may occur, necessitating the periodic disassembly of the furnace tube for cleaning. Hydrofluoric acid is effective for this purpose.

Analytical specimens are stored in a horizontal side arm near the top of the furnace assembly. Several samples may be analyzed in a series. They are manipulated by magnets or by a soft iron push rod and are dropped down the guide tube to the furnace singly for each individual analysis.

The furnace itself is closed at the bottom by means of a large, standard taper, ground glass cap, sealed with low vapor pressure wax.

To obviate the condensation of metallic films, the gases must be removed from the furnace region as rapidly as possible. Large diameter tubing is used to permit

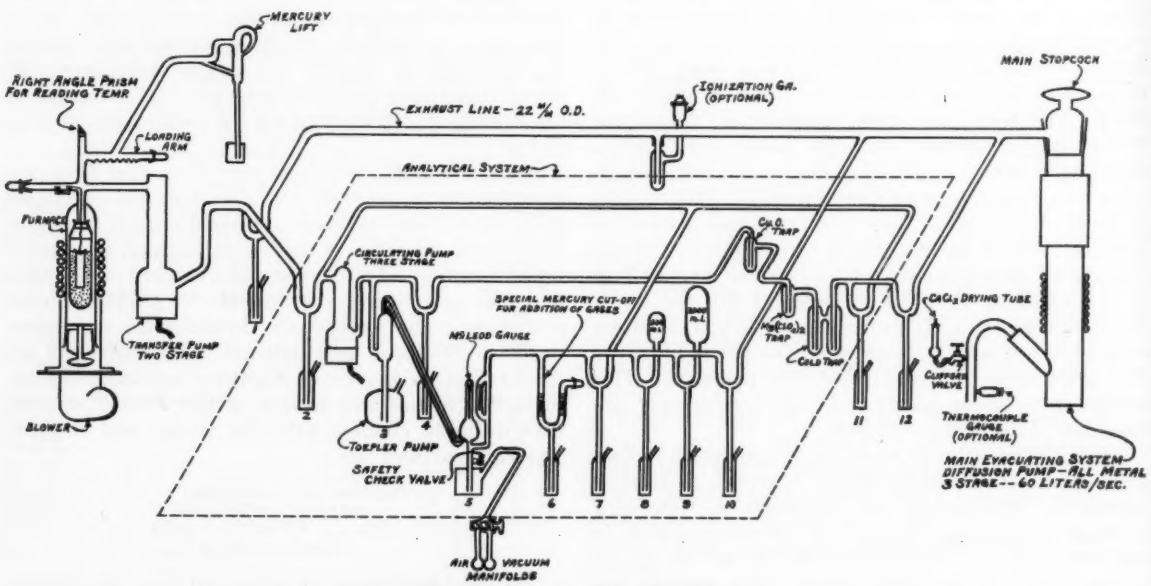
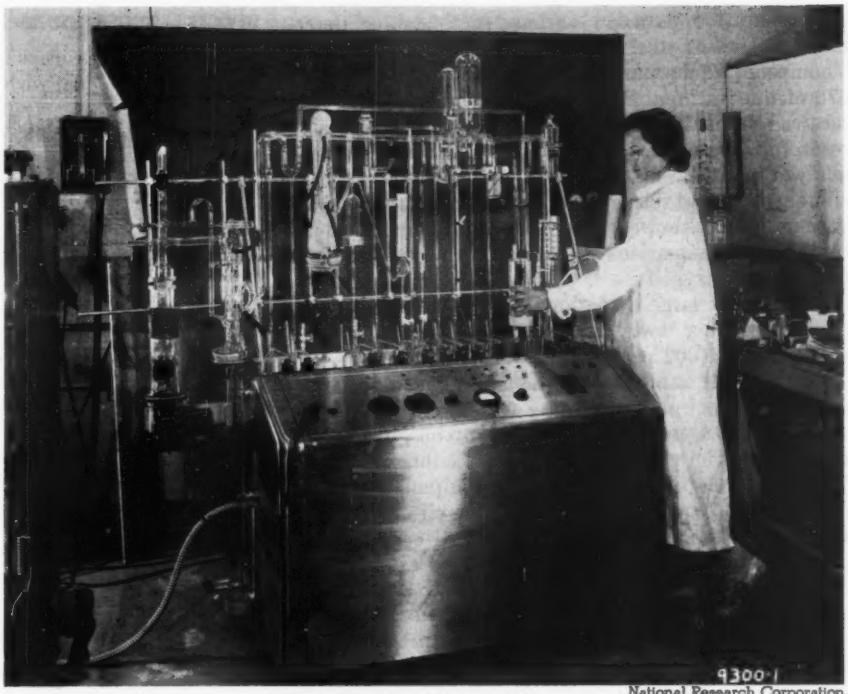


Figure 1. Vacuum Fusion Apparatus

rapid flow. By rapid evacuation of the evolved gases, moreover, the consequent lowering of the partial pressure of the gas above the liquid surface affords faster extraction of a given amount of gas from the sample and thus reduces the time-dependent "blank" correction.

Mercury diffusion pumps are usually used to evacuate the furnace. Such diffusion pumps consist essentially of a water-cooled jacket in which a suitable boiler and nozzle assembly is arranged so that mercury is ejected at high velocity in a downward direction against the cold jacket and recondensed. Gas molecules entering the jet from the upper region become entrained in the mercury vapor stream and are carried to the lower region of the pump where they are removed by a second (backing) pump, generally of the mechanical type. Diffusion pumps, built as multistage devices having several nozzles in cascade, are used advantageously. Oil diffusion pumps operate in an identical manner. However, oil diffusion pumps are unsatisfactory for the purpose of evacuating the furnace because (*a*) extracted gases build up pressures in the collection system higher than the pumps can handle; (*b*) gaseous products may be produced by pyrolytic decomposition of pump oil; and (*c*) oil vapors may diffuse back into the furnace and react with the hot crucible and the molten steel. Mercury diffusion pumps can operate against higher backpressures and do not suffer from these other disadvantages. Glass pumps are commonly employed although metal pumps have been used with satisfactory results.



National Research Corporation

Figure 2. Vacuum Fusion Apparatus

GAS ANALYSIS

After the system has been sufficiently outgassed and a satisfactory "blank" has been obtained, a specimen is introduced into the furnace. The gases evolved are then collected in the analytical system or in storage reservoirs. Some investigators, Mallett (*7*), Sloman (*9*), and others, have transferred the collected gases to conventional chemical gas-analysis apparatus for separation and measurement. However, this technique requires that macroquantities of gas be available. A more straightforward method that has been widely adopted incorporates the analytical system directly into the apparatus, as shown diagrammatically in Figure 1.

A second mercury diffusion pump is installed within the analytical system to circulate the gases through the various components. The paths taken by the gases, of course, are controlled by opening or closing the suitable cut-off valves.

In an analysis for all three gases, nitrogen, oxygen, and hydrogen, the volume of the gases collected is first measured in the McLeod gage. The gases are then passed through a trap containing hot, activated cupric oxide which oxidizes the carbon monoxide and hydrogen to carbon dioxide and water, respectively. The hydrogen, as H_2O, is removed by freezing out in a dry ice trap or by absorption in a magnesium perchlorate $Mg(ClO_4)_2$, trap. The latter has been found to be very efficient and much more convenient. Carbon dioxide is then removed on passage of the remaining gas through a trap cooled by means of liquid nitrogen. The residual gas is nitrogen; it is pumped into the McLeod gage, its volume is measured, and its quantity computed. The liquid nitrogen is then removed from its trap; the CO_2 evaporates and is measured similarly. Knowing the total volume of the evolved gas, the volume of the hydrogen is determined by difference.

ACCURACY

The accuracy of results obtained using the vacuum fusion method is only fair, but substantially better than other types of procedures. McGeary, Stanley, and Yensen (*6*) report "routine accuracy of ± 0.001 per cent"; Mallett (*7*) reports similar results. The figures of these investigators refer to absolute error. In terms of relative error, the accuracy here reported is in the range of 90 per cent.

Comparative data on various methods for determining gases in steel samples have been compiled by Thompson, Vacher, and Bright (*10*) in Research Paper 976 of the National Bureau of Standards. Data were received from 35 cooperating laboratories comprising results on more than 2000 separate determinations to analyze eight standard lots of steel for their oxygen content. Acceptable results for oxygen from these various reports showed relative errors as much as 29 per cent in high manganese steel and as much as 200 per cent for very low oxygen steel. It should be borne in mind, however, that large deviations such as this last actually represent a deviation from the mean value of a total of only 0.002 per cent oxygen.

Of the eight analytical methods employed to determine oxygen, only two were adequate to permit a selection of representative values. These were the vacuum fusion and the aqueous-iodine methods. Varying types of vacuum-fusion equipment yielded results within an acceptable value for all eight steels. In general, the range of results varied considerably. The authors attributed this to individual experimental error rather than to variations in apparatus. The four vacuum fusion procedures that yielded acceptable results had the following three characteristics in common: (1) low "blank" corrections (less than 0.001 per cent oxygen in a determination); (2) precautions against interference from manganese; (3) precautions against interference by spattering of molten metal.

The results of the vacuum fusion method are in better agreement among themselves than those obtained by the aqueous-iodine method. Further, the latter method requires more complicated procedures, a greater number of operations for each analysis, and a substantially greater amount of time.

In the interest of reducing the "blank" determination, some investigators practice "flaming" of the equipment during initial outgassing to remove gases which may be adsorbed on the inside surface of the glass envelope. Others consider this unnecessary in ordinary analyses and even undesirable. The tendency of the apparatus to return to equilibrium by readsorption of the gases may tend to lower results on the first analysis after flaming, and subsequent analyses receive no benefit from this procedure.

The size of the sample to be analyzed will be dependent on the design of the particular apparatus in use. Generally about one-half to one and one-half grams is needed, dependent on the gas content. With some techniques, particularly those in which the collected gases are transferred to an Orsat or other apparatus for analysis, larger samples are needed because a larger volume of gas is desired.

The ideally shaped sample is that which has the smallest possible ratio of surface area to mass. Excellent results can be obtained from cubic or rectanguloid specimens. The specimen is cleaned by polishing on emery paper and washing in benzene, acetone, or carbon tetrachloride. It is weighed and stored in a desiccator until it is introduced into the vacuum system.

SPECIAL TECHNIQUES

The procedures used in the vacuum fusion method are modified to deal with particular metals. The difficulty presented by the low solubility of carbon in certain metals, such as nickel, cobalt, and copper, may be overcome by fusing the sample in a bath of some previously degassed metal in which carbon is readily soluble. Iron or low-carbon steel, tin, or platinum are used for this purpose.

Vacuum Fusion Analyses of Bureau of Standards Cooperative Steels

(*a*) *NBS Coop. Steel No. 4*

	Nitrogen	*Oxygen*	*Hydrogen*
Acceptable values[a] →	2.0 to 8.0×10^{-3}	1.0 to 4.0×10^{-3}	1.0 to 3.0×10^{-4}
1	5.1×10^{-3}	2.4×10^{-3}	2.7×10^{-4}
2	2.9×10^{-3}	2.6×10^{-3}	1.8×10^{-4}
3	3.4×10^{-3}	2.1×10^{-3}	1.6×10^{-4}
4	3.2×10^{-3}	2.2×10^{-3}	1.4×10^{-4}
5	5.1×10^{-3}	2.3×10^{-3}	
6	2.9×10^{-3}	3.6×10^{-3}	
7	3.3×10^{-3}	1.9×10^{-3}	
8	4.1×10^{-3}	2.5×10^{-3}	
9	4.5×10^{-3}	2.6×10^{-3}	
10	3.4×10^{-3}	2.0×10^{-3}	

(*b*) *NBS Coop. Steel No. 6*

	Nitrogen	*Oxygen*	*Hydrogen*
Acceptable values →	3.0 to 6.0×10^{-3}	5.0 to 8.0×10^{-3}	0.4 to 3.0×10^{-4}
1	5.9×10^{-3}	4.6×10^{-3}	
2	4.0×10^{-3}	6.1×10^{-3}	
3	3.3×10^{-3}	6.4×10^{-3}	
4	4.5×10^{-3}	5.5×10^{-3}	
5	2.4×10^{-3}	6.8×10^{-3}	3.41×10^{-4}
6	3.4×10^{-3}	6.4×10^{-3}	0.59×10^{-4}
7	2.9×10^{-3}	6.5×10^{-3}	0.54×10^{-4}
8	4.6×10^{-3}	5.5×10^{-3}	0.52×10^{-4}
9	4.6×10^{-3}	6.0×10^{-3}	
10	4.0×10^{-3}	7.1×10^{-3}	
11	4.1×10^{-3}	7.8×10^{-3}	
12	2.9×10^{-3}	5.7×10^{-3}	

[a] Values given in weight per cent.

Manganese is a difficult impurity in the analysis of steel. Its high vapor pressure leads to its rapid volatilization, whereupon it condenses upon the cooler portions of the furnace and "getters" the gases evolved later. The presence of as little as 0.5 per cent Mn in a sample presents such a threat. Early investigators found it necessary to keep the Mn content of the sample low by using a large steel bath. Later workers overcame this difficulty by the addition of metallic tin. Aluminum, magnesium, and titanium in steel samples present similar problems.

Walter (*11*) has found that in the analysis of pure titanium the "gettering" characteristics can be nearly completely eliminated by dissolving the titanium sample in molten tin before the carbide reaction is initiated. This brings the titanium into more intimate contact with the walls of the graphite crucible and eliminates the difficulty encountered when the metal sample sinters and seals the voids before all the carbon monoxide has escaped. Oxygen recovery is better than

97 per cent. Stanley, vonHoene, and Weiner (*12*) also make use of tin in their melts of dilute zirconium metal in iron, and report that additions up to 25 per cent of tin appear to facilitate the reduction of zirconium oxide. The role of tin in this connection is not clear. It is believed that it may in some way affect the fluidity of the molten charge and lead to more rapid reaction of the carbon with the oxide.

Some substances, such as aluminum and silicon, have "wetting" tendencies at high temperatures. Above 1150°C. aluminum wets the crucible wall and seeps in, forming the carbide. The carbide, having a larger molecular structure, disrupts the crucible and the melt forms a pasty mass of carbide which is solid at this temperature. This effect is avoided with aluminum by keeping the temperature below 1100°C., and below appropriate upper temperature limits with other metals which exhibit similar behavior.

Samples having relatively high gas contents contribute some difficulty by tendencies to spatter as a result of the rapid evolution of gas. Careful control of the rate of temperature rise, particularly during initial stages, obviates this effect.

SOME RESULTS

Most investigators have designed and built their own apparatus. This is an involved procedure and requires the services of an expert glassblower. Until recently there was no alternative. At the present time an apparatus is being manufactured and offered commercially (National Research Corporation, Cambridge, Massachusetts) which has proved itself an adequate and useful piece of equipment. It is shown in Figure 2. As with all such apparatus, constant maintenance and occasional modification require that the operator be, or have at his disposal, a moderately competent glassblower.

It is this type of equipment which has been installed in Watertown Arsenal Laboratory. The results of a typical series of analyses are shown in the table. The data therein shown were obtained in the analysis of samples of Bureau of Standards Cooperative Steels Nos. 4 and 6, two of the eight Cooperative Steels used in the study previously referred to. These are common low-carbon steels. The analysis of these and other steel samples presents no particular difficulty and may be carried out in a routine manner. All values given are in weight per cent of gas. The table is divided into three columns, one for each of the elements of interest. The top line in each column shows the "acceptable range" of gas content as established by the Bureau of Standards from their study. Since the various gaseous components are present in such minute quantities and may be unevenly distributed throughout the bars, such an "acceptable range" necessarily prevails over any hard and fast "true value." In view of the probable heterogeneity of the steel bars, the precision obtained is considered good.

Inspection of the table will show that in all but three cases the results obtained were within the "acceptable range." These three cases were all nitrogen determinations and were all slightly low. Oxygen and hydrogen determinations made on these same specimens were within the "acceptable range." This is significant in that the analytical technique employed favors the greater accuracy of nitrogen determinations. In view of the circumstances, these deviations probably represent genuine variations in nitrogen content of the samples. This assumption is further supported by the fact that since nitrogen is measured as a residual gas after hydrogen and oxygen components have been removed, any non-condensable inert gas, such as argon, would be measured and determined as nitrogen, resulting in high, rather than low, nitrogen values.

Because of the relatively broad range of "acceptable" values, any extensive statistical discussion of the accuracy or precision of these results would not be meaningful.

While the accuracy of the vacuum fusion method is only fair, relatively, compared to that obtained in more common analytical procedures, there is no more practical, more efficient, or more reliable method yet developed for the determination of gases in metals.

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PAPER CHROMATOGRAPHY FOR STUDENTS

R. QUENTIN BLACKWELL and LEONARD S. FOSDICK
Northwestern University Dental School, Chicago, Illinois

OVER a period of several years various techniques of simplified one-dimensional paper chromatography have been used in our biochemistry classes in the Dental School and University College. Several articles on the subject have appeared in THIS JOURNAL (*1–10*); reference can also be found in review articles and manuals (*11, 12*). We have found the method described below to be the easiest to execute successfully under usual laboratory conditions. The same method has been useful in research problems where screening a number of solvent systems at different temperature conditions has been necessary to establish optimum conditions for the successful separation of various mixtures.

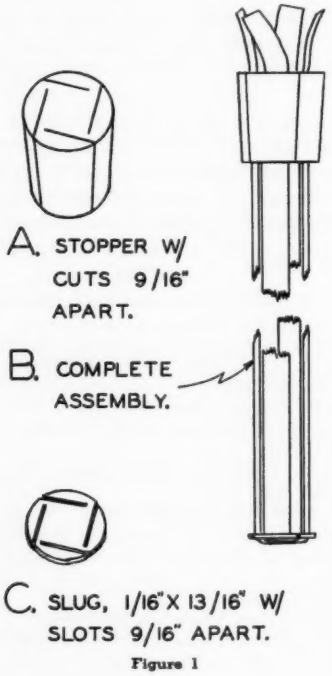

Figure 1

The method allows the analysis of four solutions in one 25 × 200-mm. test tube. This is accomplished by the use of a slotted stainless steel slug which acts both as a guide and a weight for the paper strips. The paper strips when properly fitted in the slots of the slug and suspended from the rubber stopper can be inserted into the test tube and developed by ascending chromatography. The rubber stopper (a No. 5 stopper fits the 25-mm. tube well) is sliced with a razor blade, knife, or scalpel to give four cuts in the stopper at right angles to each other; these cuts match the slots in the steel slug. The paper strips are fastened into the stopper by springing open the stopper cuts and inserting the strips. The illustrations in Figure 1 show the arrangement of the slots in the steel slug and the corresponding cuts in the rubber stopper as well as the complete setup.

The paper used for this work is Eaton and Dikeman No. 813, furnished by the manufacturer in rolls of 8 mm. width and several hundred feet long. Two 19-in. lengths of the paper are issued to each student who sets them up according to the following instructions furnished in his mimeographed laboratory manual.

(1) Obtain two strips of 8-mm. width filter paper, each 19 in. long. Avoid unnecessary handling of the strips since finger marks are ninhydrin-positive. Using a pencil apply marks to the paper at the following successive intervals from one end of the paper strips: 2 in., $6\frac{1}{2}$ in., $\frac{3}{4}$ in., $\frac{9}{16}$ in., $\frac{3}{4}$ in., $6\frac{1}{2}$ in. The last mark is almost 2 in. from the other end of the strip. Bend each strip at the $\frac{9}{16}$-in. mark to form a U-shaped strip.

(2) Insert the two U-shaped strips into the cuts in the rubber stopper so that the pencil marks 2 in. from each end are at the bottom of the stopper.

(3) Attach the steel slug to the bottom of the U-shaped strips. Make certain that all four lengths of paper between the slug and the stopper are of equal length so that the weight of the slug holds all of the strips taut. Lower the assembly into the 25 × 200-mm. test tube in order to make certain that the slug comes within $\frac{1}{2}$ in. of the bottom of the tube.

(4) Using wooden applicator sticks apply the solutions to be analyzed to the strips at the marks which are $\frac{3}{4}$ in. above the steel slug. (Practice applying the solutions to a piece of ordinary filter paper before attempting to apply them to the paper strips. The spots when properly applied should have a diameter less than the width of the paper.) Label each strip with the number of the solution placed upon it; this can be done best on the portion of the strip extending above the stopper. Allow the spots to dry for 5 minutes before inserting the assembly into the test tube.

(5) Place 5 ml. of solvent (butanol-acetic acid-water, 4:1:2 by volume) in the test tube with a pipet so that the sides of the tube are not wet by the solvent.

(6) Insert the strips into the test tube. The steel slug should dip into the solvent about $\frac{1}{8}$ to $\frac{1}{4}$ in. The point of application of the solutions must be safely above the level of the solvent. The rubber stopper should fit firmly in the test tube to make the unit vapor-tight. Place the tube in an upright position (a conical flask provides the necessary support) and allow the solvent to rise in the strips for approximately two hours.

(7) Remove the assembly from the test tube, mark the solvent boundary on each strip, and allow the strips to dry for 10 minutes.

(8) Spray the strips in the hood with ninhydrin solution. The solution consists of 0.25 g. of ninhydrin dissolved in a mixture of 90 g. of *n*-butanol and 10 g. of phenol. The strips when properly sprayed should be visibly moist; however, excess moisture may cause the amino acid bands to spread.

(9) Carefully heat the strips over a hot plate for about one minute, when spots will appear. Avoid overheating.
(10) Mark the middle of each spot, measure the distance of each mark from the original point of application of the solution, and determine the Rf values. The Rf is simply the ratio of the distance traveled by each band over the total distance traveled by the solvent.
(11) Compare the Rf value of the band of each unknown with those of the bands in the mixture and identify the unknowns.

The solutions used in the experiment are one mixture of amino acids and three solutions containing one amino acid each. The identities of the three amino acids are unknown to the student, who identifies them by their Rf values as compared to the values found in the known mixture. The approximate Rf values of each amino acid in the mixtures are given to the students in order that they may identify the individual spots on the completed chromatogram of the mixture. The amino acids used for the mixture are glycine, lysine, proline, valine, and leucine; these separate well in the butanol-acetic acid-water solvent.

Ordinarily one of the laboratory instructors sprays the strips for the students. The sets of strips still mounted with the steel slug and rubber stopper are hung from nails set in a horizontal board in the fume hood.

The ordinary atomizer is not very satisfactory for spraying because it throws some droplets along with the mist, resulting in a splotched appearance of the strip. One of the spraying flasks supplied commercially specifically for spraying paper chromatograms may be used or one may be built. We have used two types and found them satisfactory for the present experiment as well as for research work. The first type, shown in Figure 2, is quite simple and has given good service (*13*). The other, shown in Figure 3, is more sturdy and somewhat easier to use. Both depend on the use of compressed air. In both cases the compressed air is blown through a capillary tube arranged in such a position that the jet of air emerging passes over a second capillary tube set approximately at right angles to the first.

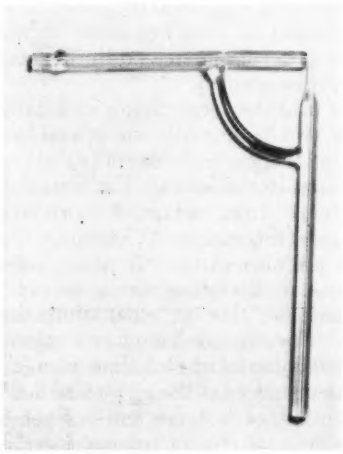

Figure 2

The second capillary tube dips into the spraying solution. The sprayer shown in Figure 2 consists of two pieces of 9-mm. Pyrex capillary tubing with a 1-mm. bore. The tubes are held in the proper position by a piece of Pyrex rod fused to them. The relative position of the two tubes for the best spray is quite critical.

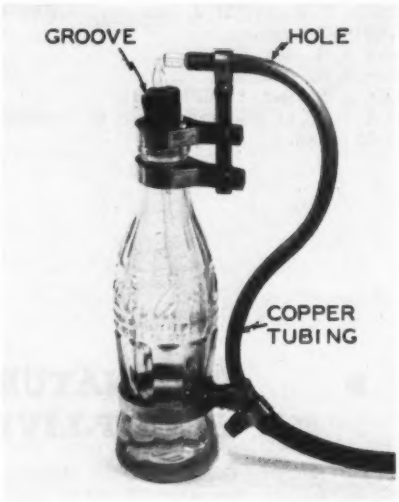

Figure 3

The sprayer shown in Figure 3 has the advantage that the relative positions of the two tubes are movable, thus allowing adjustment to provide the optimum spray. The latter sprayer was formed from a combination of $^3/_8$-in. i.d. copper tubing and 9-mm. Pyrex capillary tubing with a 1-mm. bore. The copper tubing serves as a convenient handle as well as the source of compressed air. The hole in the tubing near the top allows escape of the compressed air when the operator wishes to interrupt the spraying; during spraying the operator places his thumb over the hole forcing the air to emerge through the end of the tube. As shown in Figure 3 the air jet is formed by a short piece of capillary tubing fastened to the copper tubing. The two tubes were joined by pulling a 2-in. piece of the capillary tubing in the flame to cause a small constriction in the tube diameter midway in the tube. Next the glass tube was inserted into the copper tubing until the end of the latter was surrounding the constricted portion of the glass tube; finally the end of the copper tube was carefully hammered to shrink it into the constriction and to form a firm friction union. The copper tube is firmly held by means of stainless steel clamps to the glass container for the spraying solution. A soft-drink bottle, because of its shape and strength, was found to be suitable as the container. The glass capillary tube which dips to the bottom of the bottle is held in place by a rubber stopper. The optimum height of this tube is adjusted by trial and error until the best spray is obtained. The rubber stopper is grooved on one side to allow ingress of air to replace the liquid withdrawn during spraying. The capillary tube in

the bottle has its upper end constricted to form an orifice of $^1/_4$ mm.

The steel slugs were punched from stainless steel of $^1/_{16}$ in. thickness in a commercial press. The slots were hand cut with the use of a hack saw.

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THE NATURAL OCCURRENCE OF SHORT-LIVED RADIOISOTOPES

ISAAC ASIMOV
Boston University School of Medicine, Boston, Massachusetts

It is well known that seven elements, namely, polonium, astatine, radon, francium, radium, actinium, and protactinium (with atomic numbers of 84, 85, 86, 87, 88, 89, and 91 respectively), occur naturally, despite the fact that the half-lives of their isotopes are so short that none can reasonably be expected to have survived over the period of the earth's existence.[1] As an extreme example, the only naturally occurring francium isotope, Fr^{223}, has a half-life of 21 minutes. The evanescence of such an isotope is illustrated dramatically when we consider that if the earth's entire substance were composed of nothing but Fr^{223}, it would take less than 2.5 days to reduce that mighty quantity to a single atom.

Francium and its sister elements nevertheless exist in the earth's crust because they are continually regenerated by the decay of certain long-lived precursors such as U^{238} and Th^{232}. They are therefore found in minute quantities in ores containing thorium and uranium. What these "minute quantities" amount to has not, to the author's knowledge, been reported in the literature. Certainly, the average student of general chemistry gets a strong impression that radium, to take a glamorous example, is extremely rare and that only a few grams of it exist on the earth. That this is a false impression can be shown quite easily.

In order to do so we must first consider the radioactive decay chains involving the atoms with atomic numbers higher than 80. Four distinct chains can exist, theoretically, and of these, three occur in nature—the uranium series, the thorium series, and the actinium series.[2] The fourth, the neptunium series, contains no member sufficiently long-lived for perceptible quantities still to exist, and so does not occur in nature. The chain has, however, been created in the laboratory and its characteristics studied.

In dealing with the decay chains as usually presented in textbooks, two factors exist which tend to confuse the student. One of these is the use of trivial names for the various isotopes in the series. For instance, there is a list of "radiums" from radium A to radium G in the U^{238} series, including radium C, radium C′, and radium C″. There are also various thoriums, mesothoriums, and actiniums in the other series, to say nothing of radium emanation, thorium emanation, and actinium emanation. These names have historical validity since they were first introduced at a time when the chemical nature of the members of the series was not known and the very concept of isotopes had not yet been established. There is no reason except inertia, however,

[1] Asimov, I., J. Chem. Educ., **30**, 398 (1953).

[2] It is usually stated that the radioactive decay chains are named after the longest-lived member in the series. If that is so, the "actinium" series is actually a misnomer, since the longest-lived member in it is not actinium but U^{235}, sometimes called actinouranium. The author suggests that the most logical names for the series are the U^{238} series, the Th^{232} series, the U^{235} series, and the Np^{237} series.

for the trivial names to be perpetuated. The student certainly has a right to know that radium B, radium D, and radium G are all isotopes of lead, with all the chemical properties of lead. Under usual teaching conditions, it is much more natural for him to think that they are isotopic (or perhaps allotropic) varieties of radium itself.

The second element of confusion introduced into the radioactive decay chains, as usually presented, is that the half-lives of the constituent isotopes are given in varying units—in seconds, minutes, hours, days, or years according to the half-life's length. (The author is not aware of any exceptions to this statement.) The result is that where it is desired to obtain ratios of half-lives—as, for instance, in the calculations introduced into this paper—preliminary conversions of one time unit into another are necessary.

Table 1
The U^{238} Series

	Element	*Nuclide*	*Half-life, seconds*
	Uranium	$_{92}U^{238}$	1.42×10^{17}
	↓α		
	Thorium	$_{90}Th^{234}$	2.08×10^{6}
	↓β		
	Protactinium	$_{91}Pa^{234}$	6.84×10
	↓β		
	Uranium	$_{92}U^{234}$	7.41×10^{12}
	↓α		
	Thorium	$_{90}Th^{230}$	2.52×10^{12}
	↓α		
	Radium	$_{88}Ra^{226}$	5.11×10^{10}
	↓α		
	Radon	$_{86}Rn^{222}$	3.30×10^{5}
	↓α		
	Polonium	$_{84}Po^{218}$	1.83×10^{2}
99.96%	↓α ↘ 0.04%		
	Lead ↓β Astatine	$_{82}Pb^{214}$	1.61×10^{3}
	Bismuth ↙α	$_{85}At^{218}$	2
99.96%	↓β ↘ 0.04%	$_{83}Bi^{214}$	1.18×10^{3}
	Polonium ↓α Thallium	$_{84}Po^{214}$	1.5×10^{-4}
	Lead ↙β	$_{81}Tl^{210}$	7.92×10
	↓β	$_{82}Pb^{210}$	6.94×10^{8}
	Bismuth	$_{83}Bi^{210}$	4.32×10^{5}
99.99999%	↓β ↘ 0.00001%		
	Polonium ↓α Thallium	$_{84}Po^{210}$	1.21×10^{7}
	Lead ↙β	$_{81}Tl^{206}$	2.54×10^{2}
		$_{82}Pb^{206}$	Stable

It seems worth while, therefore, to present the four radioactive decay chains in Tables 1, 2, 3, and 4, with these two elements of confusion eliminated. The actual name of the element and the actual isotope symbol is given for each member of the chain, and the half-life is presented uniformly in seconds. The data on which Tables 1 to 4 have been constructed are from Glasstone's monograph.[3]

To determine the actual quantity of any of these radioactive isotopes in the earth's crust, it is necessary to make use of the principle that at radioactive equilibrium the number of atoms present of each of the chain's constituent isotopes is directly proportional to

[3] GLASSTONE, S., "Sourcebook on Atomic Energy," D. Van Nostrand Co., New York, 1950.

Table 2
The Th^{232} Series

	Element	*Nuclide*	*Half-life, seconds*
	Thorium	$_{90}Th^{232}$	4.38×10^{17}
	↓α		
	Radium	$_{88}Ra^{228}$	2.11×10^{8}
	↓β		
	Actinium	$_{89}Ac^{228}$	2.21×10^{4}
	↓β		
	Thorium	$_{90}Th^{228}$	5.99×10^{7}
	↓α		
	Radium	$_{88}Ra^{224}$	3.14×10^{5}
	↓α		
	Radon	$_{86}Rn^{220}$	5.45×10
	↓α		
	Polonium	$_{84}Po^{216}$	1.6×10^{-1}
99.986%	↓α ↘ 0.014%		
	Lead ↓β Astatine	$_{82}Pb^{212}$	3.82×10^{4}
	Bismuth ↙α	$_{85}At^{216}$	3×10^{-4}
66.3%	↓β ↘ 33.7%	$_{83}Bi^{212}$	3.63×10^{3}
	Polonium ↓α Thallium	$_{84}Po^{212}$	3×10^{-7}
	Lead ↙β	$_{81}Tl^{208}$	1.86×10^{2}
		$_{82}Pb^{208}$	Stable

the respective half-lives. Where there is a branch in the decay chain, the number of existing atoms of the branched product, as determined from half-life ratios, must be multiplied by the fraction of the total decay of its precursor which is given over to its own formation. Thus, in the Th^{232} series the number of atoms of At^{216} is related to the number of atoms of Th^{232} by multiplying the latter by the factor:

$$\frac{3 \times 10^{-4}}{4.38 \times 10^{17}} \times 0.00014$$

Thus, if the total quantity of existing uranium, thorium, and neptunium is known, the problem of the total quantity of the daughter isotopes becomes one of simple arithmetic.

Neptunium may be dismissed immediately as not existing in nature. It has been estimated, however,

TABLE 3
The U^{235} Series

	Element	*Nuclide*	*Half-life, seconds*
	Uranium	$_{92}U^{235}$	2.23×10^{16}
	↓α		
	Thorium	$_{90}Th^{231}$	8.86×10^{4}
	↓β		
	Protactinium	$_{91}Pa^{231}$	1.01×10^{12}
	↓α		
	Actinium	$_{89}Ac^{227}$	6.84×10^{8}
98.8%	↓β ↘ 1.2%		
	Thorium ↓α Francium	$_{90}Th^{227}$	1.63×10^{6}
	Radium ↙β	$_{87}Fr^{223}$	1.26×10^{2}
	↓α	$_{88}Ra^{223}$	9.68×10^{5}
	Radon	$_{86}Rn^{219}$	3.92
	↓α		
	Polonium	$_{84}Po^{215}$	1.83×10^{-3}
99.9995%	↓α ↘ 0.0005%		
	Lead ↓β Astatine	$_{82}Pb^{211}$	2.17×10^{3}
	Bismuth ↙α	$_{85}At^{215}$	1×10^{-4}
99.68%	↓β ↘ 0.32%	$_{83}Bi^{211}$	1.30×10^{2}
	Polonium ↓α Thallium	$_{84}Po^{211}$	5×10^{-3}
	Lead ↙β	$_{81}Tl^{207}$	2.86×10^{2}
		$_{82}Pb^{207}$	Stable

that the uranium content of the lithosphere is 0.008 per cent,[4] while the corresponding figure for thorium is 0.002 per cent. If we restrict ourselves to the dry land area of the earth and take only the outermost mile as the only portion whose mineral content is likely to be useful to mankind in the foreseeable future, we are left with a portion of the lithosphere which (assuming a density of 2.7) has a mass of 6.70×10^{23} g. The mass of the constituent thorium, Th^{232}, is therefore 1.34×10^{19} g., while that of uranium is 5.36×10^{19} g. Since uranium is composed of U^{238} and U^{235} atoms in the ratio 9929:71, the mass of U^{238} is 5.32×10^{19} g., while that of U^{235} is 3.80×10^{17} g.

TABLE 4
The Np^{237} Series

Element	*Nuclide*	*Half-life, seconds*
Plutonium	$_{94}Pu^{241}$	3×10^{8}
↓β		
Americium	$_{95}Am^{241}$	1.58×10^{10}
↓α		
Neptunium	$_{93}Np^{237}$	6.94×10^{13}
↓α		
Protactinium	$_{91}Pa^{233}$	2.37×10^{6}
↓β		
Uranium	$_{92}U^{233}$	5.11×10^{12}
↓α		
Thorium	$_{90}Th^{229}$	2.21×10^{11}
↓α		
Radium	$_{88}Ra^{225}$	1.28×10^{6}
↓β		
Actinium	$_{89}Ac^{225}$	8.64×10^{5}
↓α		
Francium	$_{87}Fr^{221}$	2.88×10^{2}
↓α		
Astatine	$_{85}At^{217}$	1.8×10^{-2}
↓α		
Bismuth	$_{83}Bi^{213}$	2.82×10^{3}
96% ↓β ↘ 4%		
Polonium ↘ α	$_{84}Po^{213}$	4.2×10^{-6}
↓α Thallium	$_{81}Tl^{209}$	1.32×10^{2}
Lead ↙ β	$_{82}Pb^{209}$	1.19×10^{4}
↓β		
Bismuth	$_{83}Bi^{209}$	Stable

From these figures and the data in Tables 1 to 4, the information in Table 5 can be calculated.

In the case of each of the seven elements listed in Table 5, the indicated isotope makes up at least 99.99 per cent of the weight of the element in the earth's crust.

[4] GUTENBERG, B., Editor, "Internal Constitution of the Earth," 2nd ed., Dover Publications, Inc., New York, 1951, p. 87.

TABLE 5
Weight of Short-Lived Isotopes Naturally Occurring in the Outermost Mile of the Earth's Land Area

Element	*Most frequently occurring nuclide*	*Total mass, grams*
Polonium	$_{84}Po^{210}$	4.00×10^{9}
Astatine	$_{85}At^{218}$	6.86×10^{-2}
Radon	$_{86}Rn^{222}$	1.15×10^{8}
Francium	$_{87}Fr^{223}$	2.45×10
Radium	$_{88}Ra^{226}$	1.82×10^{13}
Actinium	$_{89}Ac^{227}$	1.13×10^{10}
Protactinium	$_{91}Pa^{231}$	1.69×10^{13}

Thus, although six isotopes of polonium exist naturally in addition to the Po^{210} of the table, their combined mass is only 6.28×10^{4} g., as compared with 4.00×10^{9} for Po^{210} alone. In the case of each element except astatine, the predominant naturally occurring isotope is also the most stable isotope. In the case of astatine, it is At^{210}, with a half-life of 8.3 hours, which is most stable but it occurs in none of the radioactive series and is completely artificial.

Note that the most common of the seven elements is radium and that the mass of radium in the limited portion of the earth's crust being considered still exceeds 18 billion kilograms. While this is certainly a trace amount if considered to be distributed throughout the volume of crust under study (of which it forms only 2.7×10^{-9} per cent by weight), it would prove to be a sizable quantity if gathered in one place. Assuming a density of 5, the radium in the earth's accessible crust would form a cube 1120 yards (12.7 city blocks) on each side. This would amount to over a quarter of a cubic mile—certainly a different picture from the usual vision of radium as an almost non-existent material.

Astatine and francium, to be sure, are trace elements even when collected in a single spot. In the three natural radioactive series, both elements occur only in branched portions of the chain, and on the heavily unfavored side of the branch at that. As a final comment, it may be interesting to note that such is the power of Avogadro's number that were the 70 mg. of existing astatine to be uniformly distributed through the upper mile of the earth's entire land surface, each kilogram of the lithosphere would, nevertheless, contain 3.5 atoms of astatine.

PLANT DESIGN FOR UNDERGRADUATE CHEMICAL ENGINEERS

MAX S. PETERS
The University of Illinois, Urbana, Illinois

OUR modern methods of engineering education involve exposing the undergraduate student to a wide variety of subjects. As the education process proceeds, the courses become more and more specialized until the student finally emerges as a mechanical, electrical, chemical, or other type of engineer. In many cases, the undergraduate engineer finishes his university training with a good grasp of the information presented in the individual courses he has taken, but he has not had the opportunity for a composite application of his knowledge. This situation may be remedied for the undergraduate chemical engineer by including a comprehensive plant-design course in the senior-year program.

The undergraduate chemical engineer takes courses in mathematics, calculus, English, chemistry, electrical and mechanical engineering, foreign languages, stoichiometry, unit operations, and industrial technology along with other related subjects. Each of these subjects is important within itself, but, before the student is sent out with a degree in chemical engineering, he should be given a chance to interrelate the various phases of his training. The course in chemical engineering plant design is ideal for this purpose. If the course is taught correctly, it finally gives the student a chance to apply the mass of theory that has been thrown at him for almost four years. Many of the seniors enter the plant-design course as boys fumbling with a variety of information which they are not too sure is practical, and they emerge as men confident of their ability to be real chemical engineers.

Despite the obvious importance of the rounding-off course in plant design, many of our universities are graduating chemical engineers with no course of this type included in their training. Some schools attempt to make up for this deficiency by including subjects such as economics or having the students work one plant design problem as a part of their industrial technology course. These substitutes are inadequate and an injustice is being done to the students and to the industrial concerns which hire these men.

The instruction in a good plant-design course should be handled by a chemical engineer who has had industrial experience or, at least, strong contacts with industry so that he realizes the over-all type of work the students will be in when they leave the university. The instructor should recognize the importance of presenting the subject matter so that the students have the opportunity to develop a practical concept of chemical engineering and its applications.

ECONOMICS

In this modern age of industrial competition, the engineer must realize that his work will be judged on the basis of its monetary return as well as its theoretical soundness. For this reason, the practical engineer should have a basic knowledge of economics. Since plant design is, in reality, the *practical* application of chemical engineering principles, it would be impossible to discuss plant design without also including economics.

Some of our chemical engineering schools have tried to present economics as a subject independent of plant design. While such a treatment is better than no course at all, much of the value is lost since the emphasis is ordinarily placed on pure economics rather than on the combination of economics with theoretical principles to give practical results. In chemical engineering work, economics and plant design are so closely interrelated that it is always advisable to consider economics and plant design as one combined subject.

METHOD OF PRESENTATION

The ideal plant-design course consists of a series of integrated lectures and practice sessions combined with one major design problem of practical significance. Two or three one-hour lecture sessions per week permit the instructor to present the important information on economics and plant design. A weekly three-hour practice session is very valuable for solidifying the students' understanding of the information presented in the lectures. The practice session should be used for class discussion and solution of typical problems related to the lectures and discussions. Since the purpose of this course is to round off the students' training and prepare them for the industrial approach to chemical engineering, these practice-session problems should not be of the usual academic type. The problems should be completely practical and the economic implications should be strongly emphasized. The students should work on the problems in groups of two or more so that they can get the feeling for sharing ideas and cooperating with their fellow workers.

The practice sessions with the accompanying class discussions and problems are essential to a good plant-design course. The lectures by themselves would not be sufficient to achieve the goal of the course. However, the lectures combined with the practice sessions give the students a chance to listen to the general information, discuss it, and then apply it.

One major plant-design problem should also be

included in the course program. The class may be given one or two months for the solution of this problem, and it should be given during the last part of the course. This major problem should be based on a practical industrial process, and it should involve a large amount of logical thinking as well as chemical engineering, economics, and plant-design principles. The short problems in the practice sessions give the students rounded ability in the various types of design applications while the major problem proves to the student that he can tackle a difficult chemical engineering subject and follow it through to completion.

The success of the chemical engineering plant-design course rests squarely on the shoulders of the instructor. Dr. L. E. Stout, Dean of Engineering at Washington University, St. Louis, has made the following statement: "Few, if any, college professors are sufficiently well informed on industrial practices to teach a course in chemical engineering design which commands the respect of practicing engineers. . . ."[1] If this statement is correct, the teaching staffs of our chemical engineering schools are not adequate for the task of preparing our young men for graduation with degrees in chemical engineering. No good school should consider itself capable of granting bachelor's degrees in chemical engineering unless it has at least one man on its staff with sufficient practical experience and understanding of industrial methods to permit him to present a respectable design course. The main point which Dr. Stout intended to bring out in his statement was that outside lecturers should be brought in from industry for the course in plant design. This suggestion has a great deal of merit and should be followed if at all possible. However, this does not mean that the entire course should be given over to a series of lectures by various industrial "experts" although this method has been used by some of our chemical engineering schools.[2] A good plant-design teacher can organize his lectures so that a fine continuity runs through the entire course. If the classes are occasionally given over to appropriate talks by capable men from industry, the students will benefit from the direct contacts with industrial ideas and practices. These outside lectures can be arranged to fit in with the subject matter previously treated by the instructor and the new viewpoints will serve as an ideal balance for the course.

Outline of Essential Material to be Covered in the Plant Design Course

I. Elementary Economic Considerations
  A. Costs
    1. Fixed costs
    2. Direct production costs
    3. General plant overhead
    4. General administrative and office overhead
    5. Distribution costs
    6. Contingencies
  B. Investments
    1. Fixed capital investment
    2. Working capital investment
    3. Total investment
  C. Depreciation
    1. Obsolescence, service life, depletion, and scrap value
    2. Straight line method for determining depreciation
    3. Reducing balance method for determining depreciation
    4. Sinking fund method for determining depreciation
  D. Return on investments
  E. Investment comparisons
  F. Cost estimates
    1. Order-of-magnitude estimates
    2. Preliminary estimates
    3. Firm estimates
    4. Labor and material indexes
    5. Multiplication factors

II. General Design Considerations
  A. Batch versus continuous processes
  B. Insurance, health, and safety requirements
  C. Fabrication of equipment
  D. Materials of construction
  E. Patents
  F. Plant location
  G. Designs for special equipment
  H. Instrumentation
  I. Waste disposal
  J. Structural design

III. The Design Project
  A. Preliminary designs
  B. Detailed estimate designs
  C. Firm process designs
  D. Design project procedure
  E. Literature surveys
  F. Comparison of different processes
  G. Flow diagrams
  H. The design report

IV. Design Calculations and Methods
  A. Transfer of materials
  B. Heat transfer
  C. Mass transfer
  D. Chemical kinetics in design
  E. Miscellaneous

OUTLINE OF COURSE

The subject material which should be covered in the plant-design course can be broken down into four general headings as follows:

I. Economic considerations.
II. General design considerations.
III. The design project.
IV. Design calculations and methods.

The table presents an outline of the important subjects that should be included under each of these four general headings.

A treatment of chemical engineering economics should be presented at the beginning of the course. This gives the students an introduction to the financial side of chemical engineering and permits an immediate visualization of the essential profit problems facing all industrial concerns. The various types of costs involved in industry along with methods for estimating these costs should be considered. Investments and return on investments are of particular importance and these two topics should be covered thoroughly before any design problems are attempted.

To present the over-all picture of plant design, it is necessary to include a number of specialized topics such as plant location, waste disposal, patents, and others

[1] STOUT, L. E., Am. Soc. Eng. Educ. address, June, 1951.
[2] NICHOLS, W. T., *Chem. Eng. Prog.*, **48**, 201 (1952).

as shown in the table. The emphasis to be placed on each of these subjects must be determined by the instructor. Time limitations may make it impossible to cover each of the general design considerations in detail; however, no course in plant design would be complete without, at least, a brief discussion of the ten general subjects indicated in the table.

The methods for carrying out a design project should be covered in detail. The various types of designs and procedures for developing the best possible processes must be discussed. Many students are very weak in preparing adequate reports on the work they have done; therefore, the treatment of the design project should include a comprehensive discussion on report writing along with samples of outlines for the various types of design reports.

Probably the most important part of the plant-design course is the portion dealing with design calculations and methods. It is here that the students have the opportunity for a composite application of their previous training. The instructor must be very careful to tie in the theoretical considerations with practical considerations. For example, in the design of a countercurrent, gas-liquid absorption tower, the theoretical principles from earlier unit-operations courses are used to estimate the height of a tower necessary for a given performance. The diameter may be determined from design data dealing with maximum allowable vapor velocities. The optimum diameter and height will depend on the gas-blower power costs necessary to overcome the pressure drop, power costs for pumping the liquid to the top of the tower, costs of fabricating the different sizes of towers, and other variables depending upon the particular process. In addition, the space available for the tower as well as constructional and material-shipping difficulties must be considered. In working with problems of this type, the students obtain a full realization of the ways of applying their theoretical training and the practical limitations set by industrial conditions.

As many of the unit operations as possible should be included when dealing with methods for design calculations. In a course of this type, it is best to cover the various unit operations under the general headings of materials transfer, heat transfer, and mass transfer. Since it is impossible to treat all the possible design calculations, the instructor must choose certain typical examples and explain them in a clear fashion. In this way, the students will see the manner in which the theoretical principles are applied to practical cases of design, and they will be able to extend these methods to other types of problems.

The class lectures on materials transfer might start with methods for determining optimum pipe diameters. This could lead easily into design of pipe lines and selection and location of pumps. Treatment of flow of fluids could be extended to include methods for estimating pressure drop or maximum allowable velocities in packed towers and bubble-cap plate towers. A discussion on the design of gas turbines and the generation of electricity would show the students how their courses in fluid flow and electrical engineering can be tied together. Methods for filtration design calculations, including power requirements for the vacuum pump motor on a continuous rotary filter, could also be included in the general treatment of materials transfer or fluid flow.

The instructor must have an organized plan for presenting the part of the course dealing with methods for design calculations. A series of isolated examples chosen with no regard for continuity will be of little value to the students. The transition from one subject to another should be made gradually so that the students have the feeling of one subject leading directly into the next.

Methods for applying chemical kinetics in design calculations should be emphasized. Too many of our chemical engineers never see the practical use of their chemical thermodynamics and kinetics courses. A few typical examples in the design class will open the students' minds to the value of chemical kinetics. Sherwood and Pigford[3] have presented a classic example of the application of kinetics to design calculations. They give a detailed explanation showing how the number of trays theoretically needed in a nitric acid absorption tower can be determined by use of reaction-rate constants for the oxidation of nitric oxide to nitrogen dioxide and equilibrium constants for the reaction between water and nitrogen dioxide. The use of this nitric acid example illustrates how a smooth transition could be accomplished from mass transfer discussions to considerations emphasizing chemical kinetics in design.

THE MAJOR PROBLEM

One of the main goals of the major design problem is to give the individual student confidence in himself and his ability as a chemical engineer. Therefore, it is best to have the students work alone on the major problem rather than in groups of two or three. The instructor must choose this problem with a great deal of care. It must be typically representative of the type of design problems encountered in industry and its solution should lead to a concise and definite result.

The National Student Contest Problem put out yearly by the American Institute of Chemical Engineers is ideal for use as the major design problem. The students are given thirty days for completion of the contest, and the winners of the top six places are given national recognition. These problems are always very well presented and are usually drawn up by men in industry.

As the senior chemical engineer goes through the early part of his design course, he begins to understand why he has had to study such a wide variety of subjects. He starts to realize that he can apply his training as a composite whole and not just in sections. The

[3] Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," 2nd ed., McGraw-Hill Book Co., Inc., New York, 1952, p. 372.

methods and problems of industry become something tangible. After the student, following many stops and starts, finally completes the major design problem, he becomes a man confident of his ability to take his place in industry as a chemical engineer.

Too many of our schools are graduating chemical engineers without tying their training together and preparing them for industry. A good course in plant design will remedy this situation. It is up to our chemical engineering schools to supply such a course.

JEAN BAPTISTE GILLIS

RALPH E. OESPER
University of Cincinnati, Cincinnati, Ohio

AMONG the contemporary Belgian chemists, Jean Baptiste Gillis is outstanding in the field of analytical chemistry. Son of a military physician, he was born at Arlon on August 8, 1893. His secondary education, along the usual classical lines, was obtained at Ghent, the home of his mother, and then at Antwerp. In 1911 he enrolled at the University of Ghent and in 1913 became a candidate for a degree in natural sciences. His chemical training was under the supervision of Frederic Swarts (1866–1940) who is well remembered for his pioneering work with fluorine compounds.[1] When the first world war broke out, Gillis immediately joined the colors and as an infantryman took part in the defense of Liège and Antwerp. He was wounded and evacuated to Holland, where in 1915 he was attached to the École Belge d'Amsterdam as instructor in physics and chemistry, since he had qualified as a teacher in these subjects.

He also attended the courses of A. F. Holleman[2] and Andreas Smits[3] at the University of Amsterdam. The former had an international reputation for his work on substitution in the benzene ring and his textbook of organic chemistry. The latter, a physical chemist, was the author of the widely known "Theories of Allotropy." Gillis started his research career in Smits' laboratory, where he studied the heterogeneous and homogeneous equilibria of two systems, namely, thiocyanates and isothiocyanates, and reducing sugars in the presence of water or organic solvents. In 1917 he reached England and then went back to the Belgian front, this time in the artillery. In September, 1918, he took the doctoral examination before the Jury Central, which had been set up by the Belgian authorities and was then meeting in Le Havre, France. His work on the thiocyanate-isothiocyanate equilibrium served as the thesis. After the Armistice in November, 1918, Dr. Gillis was given a post in the laboratory of general chemistry at Ghent. It was directed by Swarts, his former teacher, who was maintaining the excellent chemical tradition which had been instituted there by Kekulé (1858–68) and continued by his father, T. Swarts, and brother-in-law, Leo Baekeland, before the latter's emigration to the United States.

In 1923 the Faculty of Sciences came to a fortunate decision; it set up an independent chair of analytical chemistry. No longer, as in the past, was it a mere dependent of the courses in general and applied chemistry; it became something higher than the "humble servant" of the other disciplines. Gillis was made the first occupant of the new chair, a position he has filled with distinction. Here he has been able to carry on researches in the theory of analytical chemistry and also to conduct studies of a practical nature, as is fitting in view of his courses for engineers, pharmacists, and those specializing in chemistry.

Since much of his training had been in physical chemistry, it was but natural that he began his independent research career with electrochemical problems; he made valuable contributions to potentiometry and rapid electroanalysis. Polarography was introduced into his laboratory in 1928. By scraping the anode and cathode simultaneously and continuously with a diamond during the electrolytic deposition of various metals, he proved the importance of the adsorption of their own ions and also contributed to a better understanding of passivity.

In the field of colloids, he made quantitative studies of the exchange of ions to negative silver iodide sol. When it was found that the determination of traces of elements was important to the preparation of this sol in a pure state, he made the necessary determinations

[1] For biographical details, see VAN HOVE, T. H., *Bull. soc. chim. Belges*, **49**, 33 (1940).
[2] See J. CHEM. EDUC., **13**, 401 (1936); JORISSEN, W. P., *Chem. Weekblad*, **15**, 1309 (1918).
[3] See J. CHEM. EDUC., **17**, 151 (1940); GILLIS, J. B., *Koninkl. Vlaam. Acad. Wetenschap. België*, **1949**, 188–206.

polarographically as well as by means of the spectrograph.

His work on the determination and toxicity of mercury vapor led him to the use of charcoal activated with five per cent of bromine as a collector for these vapors.

With the aid of several collaborators he sought to prove in general that in spectrochemistry it is possible to determine not only the minor elements but also the metals which are present in predominant proportions. This program was applied with success to white metal, bronze, steel, clay, and blast-furnace slag. For the past several years his laboratory has been equipped for the direct analysis of special steels and the feasibility of the original idea has been sustained.

In 1940 Professor Gillis was appointed to the Committee on Analytical Reactions of the International Union of Pure and Applied Chemistry.[4] He then embarked on an extensive program of studying critically the reactions of analytical chemistry. Together with C. J. van Nieuwenburg (Delft) and Paul Wenger (Geneva) he issued the well-known "Deuxième Rapport" (Basle, 1945) whose essence was contained in the "Reagents for Qualitative Inorganic Analysis" (New York, 1948) by Wenger, Gillis, and van Nieuwenburg. As chairman of the commission he is now directing the critical and experimental study of the reactions of colorimetry.

The graphical representation of the sensitivity of reactions and the effect of foreign materials on sensitivity have led him to construct many sensitivity diagrams and to employ them, for example, for semiquantitative purposes under conditions which are quite simple with respect to both material and execution.[5]

During the more recent years he has devoted himself mostly to the synthesis of new organic reagents designed for the sensitive detection of certain ions. For example, cuproine has been the subject of a very nice study which has resulted in a specific test for univalent copper. A most fertile field has been opened, particularly by his collaborator, J. Hoste, who has been studying the steric blocking of the functional group of ferrone and cuproine by terminal groups, and there is hope that it may become possible to choose and construct reagents on more rational bases of both physical and chemical nature.

Not all of Professor Gillis' fields of research have been touched on here, but enough has been given to prove that he is an exceedingly effective member of the chemical profession. He is Associate Editor of *Analytica Chimica Acta.*

[4] See J. CHEM. EDUC., **30**, 66 (1953).

[5] *Ibid.*, **29**, 170 (1952).

TYGON BULBS FOR MEDICINE DROPPERS

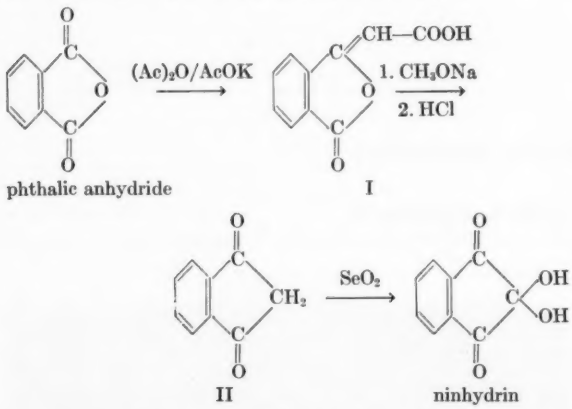
JOHN L. MARGRAVE
University of Wisconsin, Madison, Wisconsin

THE deterioration of rubber bulbs on medicine droppers is a common problem in the semimicro analytical laboratory and the advantages of bulbs made of Tygon, polyethylene, or some other flexible material which is resistant to the action of most common reagents are apparent. The illustration shows a medicine dropper fitted with a "bulb" of 1/4-inch Tygon tubing. The end was sealed by heating with an ordinary soldering iron fitted with a special tip designed to hold the tubing tightly closed while being heated. Droppers fitted with bulbs of this type have given good service in our student laboratories when used with a variety of common laboratory reagents—dilute and concentrated acids, ammonia solutions, NaOH solutions, and so forth.

THE PREPARATION OF NINHYDRIN AS A LABORATORY EXPERIMENT

XORGE ALEJANDRO DOMINGUEZ
Instituto Tecnologico y de Estudios Superiores de Monterrey, Monterrey, Mexico

NINHYDRIN (triketohydrindene hydrate) is a very useful colorimetric reagent for the identification and analysis of amino acids (*1*, *2*, *3*) and its use has been extended to the paper chromatography of amino acids and protein hydrolyzates (*4*). Several simplified techniques for the use of this reagent in undergraduate biochemical and organic experiments have been proposed (*5*). Unfortunately ninhydrin is very expensive, but it can be synthesized by any undergraduate student in three laboratory sessions, some very interesting reactions being involved. Starting with cheap phthalic anhydride, which is condensed with acetic anhydride using potassium acetate as catalyst (*6*) (pyridine is inactive), the phthalylacetic acid (I) obtained is converted to 1,3-hydrandione-carboxylic acid with a methanol solution of sodium methoxide. This carboxylic acid is decomposed with hydrochloric acid and the 1,3-hydrindanedione (II) obtained is oxidized with selenium dioxide (*7*) to ninhydrin, which is then purified (*8*).



phthalic anhydride — I — II — ninhydrin

Preparation of Phthalylacetic Acid. A mixture of 40 ml. of acetic anhydride, 30 g. of phthalic anhydride, and 5 g. of potassium acetate was heated to 155–65° in an oil bath for 15 minutes. The mixture changed color from yellow to reddish violet. Then the mixture was poured into ice-cold water, and the yellow precipitate was collected by suction and rinsed several times with water and once with a small amount of 50 per cent alcohol solution. After drying, the precipitate weighed 16–20 g. (41–51.5 per cent yield) and its melting point was 210–27°. A sample of crude phthalylacetic acid was crystallized from hot methanol, giving yellow needles melting at 244–6° (theoretical m. p. 246°).

Preparation of 1,3-Hydrindanedione. To a solution of 14.3 g. of sodium methoxide (or its equivalent obtained by dissolving sodium in methanol) in 200 ml. of anhydrous methanol was added 15 g. of phthalylacetic acid, the red solution was allowed to stand one hour at room temperature, then the yellow precipitate was collected by suction and mixed with 150 ml. of a 10 per cent solution of sulfuric acid. This mixture was heated on the steam bath until no more carbon dioxide was evolved (15–20 minutes), the hot solution was filtered and allowed to cool, and the yellow crystals of 1,3-diketohydrindanedione were collected by suction, rinsed with water, and dried (m. p. 124–6°). A sample was recrystallized from ligroin, melting at 129–30°. The yield was 4–7 g. (35–67 per cent).

Preparation of Ninhydrin. A solution of 3.1 g. of selenium dioxide (or its equivalent of selenious acid) in a mixture of 66 ml. of dioxane and 1.2 ml. of water was heated to approximately 60–70°, then 4 g. of crude 1,3-diketohydrindanedione was added, and the resulting mixture was refluxed five hours. The hot mixture was filtered and concentrated to one-fourth of its volume on the steam bath, and then 20 ml. of water was added and the solution was boiled to coagulate the red tarry precipitate which was removed by filtration. The filtrate was boiled with 0.2 g. of Norite, filtered again, concentrated to 6–8 ml. and allowed to stand at room temperature. The crystals of crude ninhydrin were collected by suction and recrystallized from 8 ml. of a 5 per cent solution of hot hydrochloric acid with the aid of 0.2 g. of Norite. Long colorless prisms of ninhydrin were obtained, melting at 239–41°, which turned red at 127–9°. With α-amino acids the characteristic blue color reaction was produced. The yield was 1.1–1.5 g. (22.5–30.5 per cent).

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PHYSICAL CHEMISTRY IN PHARMACEUTICAL RESEARCH[1]

J. M. VANDENBELT
Parke Davis and Company, Detroit, Michigan

THE physical chemistry of the modern pharmaceutical laboratory is to some extent a complicated analytical chemistry. Recent developments in the field range from seemingly simple techniques, using old and familiar materials, to relatively expensive and elaborate arrangements, employing the very latest developments in the fields of optics and electronics. So varied and valuable have these techniques become during the last decade that sizable laboratories usually have a group charged principally with the responsibilities for these operations.

It usually requires several months for an operator to become thoroughly familiar with a new technique. It may take as many years to acquire an adequate background and experience in the interpretation of data. It is by combination of these manipulative skills with the specialized experience that the finest yield in investigative return is obtained.

A specific example of the contribution that a physical method may make is shown in the determination of the structure of the antibiotic A-65, Chloromycetin.

[1] Presented at the 49th meeting of the Michigan College Chemistry Teachers Association, May 9, 1952.

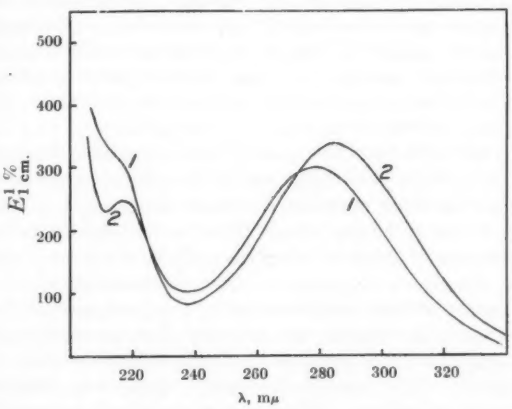

Figure 1

Curve 1: A-65
Curve 2: *p*-nitrotoluene O_2N⟨⟩CH_3 (ord. × 1/2)

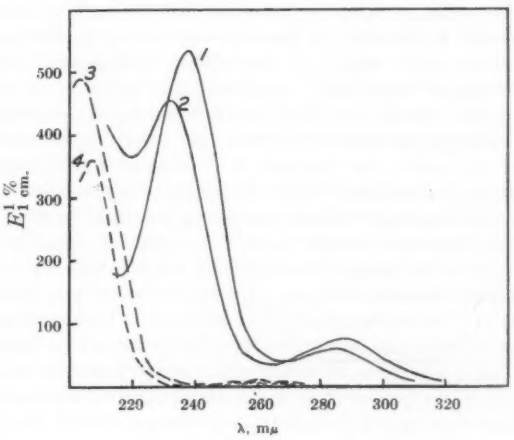

Figure 2

Curve 1: A-65 reduction
Curve 2: *p*-toluidine (ord. × 1/2)
Curve 3: A-65 red. in HCl
Curve 4: *p*-toluidine in HCl (ord. × 1/2)

Figure 1 shows the ultraviolet absorption spectrum of the antibiotic. From experience with many types of spectra, it would seem that the characteristics resemble most closely those of a nitrobenzene derivative. For comparison, the curve of *p*-nitrotoluene is given in the figure. The similarity in band shapes and positions of the two curves indicates that the chromophores are closely related. To test the nitrobenzene hypothesis, a simple chemical reduction was performed on the antibiotic. This should give the amino derivative similar in chromophoric properties to *p*-toluidine. The solid curves in Figure 2 show a convincing similarity. As a further check, both reduction product and *p*-toluidine were examined in strongly acid solution. Again there is a striking agreement, indicating that indeed the antibiotic contains a *p*-nitrobenzyl group. A sizable portion of the structure of the new compound was thus established in a few hours.

CHEMISTRY TEACHING FOR GENERAL EDUCATION[1]

WILLIAM HERED
Indiana University, Bloomington, Indiana, and
University of Chicago, Chicago, Illinois

In those institutions having no distinct program of general education the beginning course in chemistry must assume responsibility for representing science as a significant aspect of intellectual activity. The need for a widely educated citizenry, rather than the narrow specialists of Plato's ideal, becomes increasingly obvious as the complexities of life grow. A real appreciation of the methods, aspirations, and limitations of science has become an essential ingredient of general education.

Too often, under the pressure of covering as much material as possible in the ever-tightening curriculum, teachers lose sight of this basic obligation. The presence of qualitative analysis, for instance, in the first year's work, has little justification except, perhaps, as training for future chemists; the resulting compression of more vital matter is extremely unfortunate. The basic problem consists in emphasizing science as a way of thinking, without sacrificing essential content.

One solution would allow the general aspects of science to be taught in a separate course, thereby permitting concentration on content in beginning chemistry. The weakness of this solution is fundamental; science has no meaning divorced from context. Clearly the rigid discipline of a particular subject matter must be the basis for any fruitful exemplification of science.

Can one afford the additional time required for increased emphasis on science in view of the other responsibilities of the beginning course? The answer is that time *must* be found, even at the risk of doing away with some of the sacred cows of tradition. Numerous topics can be excised without harm either to preprofessional training or to education for life.

While the most significant efforts in the direction of education in the meaning of science are represented by the integrated studies, there is no reason why such efforts cannot be made successfully within the format of the first-year specialized course. The content need not be revised drastically; the major alteration would be in the way of viewing the content. A critical and inquiring attitude toward the problems encountered and constant vigilance for *lacunae* in the reasoning process should provide the proper atmosphere. The textbook or syllabus should exhibit the thought processes of the investigators, as does the physics text of Taylor (*1*).

Much can be learned about possible avenues of approach from an examination of current experiments in the integrated curricula. A brief résumé of several techniques in present use may be of value in adapting conventional materials for this approach.

One technique is that found in the much-castigated "survey" course. Integration is its professed aim, although compartmentalization usually is present. At its worst the survey is superficial, trivial, and unscientific, but at its best its promise exceeds that of the specialized courses, since the survey can draw upon a wide range of subject matter for illustrations of scientific investigation. A valuable textbook in the survey field is that of Krauskopf (*2*).

More radical departures from convention result from the application of the premise that students best learn about science by study of original reports of scientific investigations. Two implementations of this premise may be mentioned here, that of Harvard University and that of the University of Chicago.

The Harvard method is based upon the principles outlined in Conant's "On Understanding Science" (*3*), and utilizes the "Harvard Case Histories in Experimental Science" (*4*) as the basis for lecture and discussion. Each of the "Case Histories" centers about a particular problem arising in the development of science and consists of a constellation of excerpts from original reports interpreted by considerable editorial commentary. While superficially similar to the Harvard approach, that of the University of Chicago differs at salient points. Instead of excerpts from original articles, entire papers are studied wherever possible (*5*). Editorialization is limited to rewording for clarity, explanation of terms, and filling gaps; practically no evaluational material is inserted. Since understanding is regarded under the latter plan to arise if student-teacher interaction is maximized, the absence of "official" interpretation has the purpose of encouraging free discussion. Obviously a greater variety of source material is possible under the Harvard system, but from the viewpoint of education as an *active* process on the part of the learner, the Chicago technique may be on surer ground.

Quite aside from the question as to possible overemphasis of the historical or philosophical aspects of science by these methods, two basic limitations appear. One is the difficulty of exhibiting a sufficiently broad panorama of content, thus necessitating extreme care that the choice of papers be truly representative.

A more serious limitation lies in the fundamental fact that scientific reports are couched, for the most part, in terms far more suitable for fellow scientists than for students. The number of usable papers is thereby severely restricted. Moreover, those which are usable are often "old," since simplicity of concepts and quantitative manipulation is an attribute of the younger phases of a science rather than of a mature science.

[1] Presented at the 123rd Meeting of the American Chemical Society, Los Angeles, California, March 16, 1953.

Hence a common criticism of courses based entirely on original reports is that the content of present-day science lacks adequate representation.

One implication of the foregoing is that presentations of the type exemplified by the Taylor and Krauskopf texts may be combined profitably with intensive study of a few key papers. A number of such papers have proved themselves highly useful for classroom discussion. Among these are Lavoisier's "Treatise on Chemistry," the Dalton, Gay-Lussac, Avogadro, Cannizzaro, Mendeleev sequence on the development of the atomic molecular theory, the van't Hoff and Arrhenius treatments of colligative properties, and Clausius' kinetic-molecular theory.

It is entirely possible, however, to impart the essential characteristics of the scientific method without recourse to such materials if the classroom procedures reflect the scientific viewpoint. Each important hypothesis should be accompanied by supporting factual evidence, and pains should be taken to exhibit all of the links, both strong and weak, in the chain of validation. Bald and unsupported statements such as "We know that the atom is mostly empty space," violate the spirit of inquiry and cannot but leave the student unsatisfied and uninformed. Of course, not all theories require exhaustive validation; some rest on an irreducible core of abstruse physico-mathematical principles and others may not be important enough for such development.

As an illustration of a way in which conventional materials may be used to illuminate the facets of scientific method, class discussion on the kinetic-molecular theory of matter might proceed as follows.

After a preliminary grounding on possible definitions of matter and its states, alternative methods for attacking the problem of its constitution are discussed. The suitability of gases for this study, in consideration of their similarity in physical behavior, is developed. Since the theory proposed by students in explanation of expansibility, diffusibility, etc., is usually the currently accepted one, an opportunity is afforded the instructor to assume the guise of a devil's advocate by proposing an alternative postulate. He may hold, for instance, that gases are made up of particles which are always in contact and which are capable of expansion and contraction under certain conditions, his purpose being to stimulate thinking. The first reaction to such an absurd idea is usually an emotional affirmation in the "correctness" of the kinetic-molecular theory. Shortly, however, even the dullest student realizes that facts, not faith, are required here; out of the confusion should come the realization that objective evidence decides scientific issues.

As the discussion continues, the need for more precise information about gases becomes apparent. Here the law $PV = kT$ is developed as a class demonstration. A check on the validity of the kinetic-molecular theory is shown to be possible by deriving a quantitative prediction from the theory and comparing this prediction with the empirical relation. The instructor now exhibits the derivation of the equation $PV = {}^1/_3\, nmu^2$, exercising great care to furnish the essential physical concepts and definitions involved and emphasizing the underlying assumptions of negligible molecular volume and interaction. The similarity of the theoretical and empirical equations is noted.

Complete correspondence of the two equations is seen to require an additional assumption, namely that absolute temperature is the outward manifestation of molecular translational kinetic energy, thereby leading to what seems to be fact-getting without experiment. Skillful guidance of the discussion should now lead to the realization that such assumptions are not amenable to direct proof but may be validated through their consistency with other facts.

At this point the class is apt to feel quite self-satisfied and certain that the Q. E. D. has been pronounced. The illusion is promptly dispelled by exhibiting data on carbon dioxide at high pressures and low temperatures. Apparently the assumptions underlying the kinetic equation must be re-examined and modified. Allowance for molecular volume and intermolecular attraction is seen to provide corrections which are of the proper direction and magnitude. Thus deviations of gases from the gas laws can furnish additional support for the kinetic theory.

The interplay of ideas during the give-and-take of informal discussion furnishes a splendid learning situation. Naturally, the instructor's preparation for sessions of this kind is far more demanding than that for the one-way flow of the lecture, but the sense of accomplishing something worth while is its own reward. The intellectual growth of the student is almost palpable.

A note of caution must be sounded, however. Unless the course examinations truly reflect the complex objectives of instruction, much of the gain may be nullified. Students are realistic above all else, and soon refuse to struggle with the less obvious aspects of scientific reasoning in the classroom if the examinations test merely for pedestrian recall of facts and solution of hackneyed numerical problems. The importance of high-level examinations cannot be overemphasized.

In the last analysis quality in teaching rests with the individual teacher. Even the murkiest materials can be illuminated to some degree by a competent and enthusiastic personality. Nevertheless there is little sense in imposing unnecessary burdens of understanding on the student. Perhaps this paper may serve by suggesting ways of facilitating the learning process and the acquisition of desirable attitudes toward science.

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CLATHRATE COMPOUNDS

SISTER MARY MARTINETTE, B.V.M.
Mundelein College for Women, Chicago, Illinois

A RELATIVELY new group of compounds has recently been reported. It was formed as a result of studies made on compounds which do not readily fall into strictly inorganic or organic groups and which do not appear to exhibit any one, or several, of the conventional types of bonding. These compounds are cage-like in nature and offer interesting features for further investigation.

As early as 1886 Mylius (*1*) made careful observations on complex compounds formed by quinol with certain volatile compounds, such as hydrogen sulfide, sulfur dioxide, and hydrogen chloride. He found these compounds to contain three or four molecules of quinol to each molecule of the other component. Further than that they presented an enigma to him. He suggested that no ordinary combination occurred between the two types of compounds but that during crystallization the quinol molecules were in some way able to lock the volatile compounds into position without chemical bonding. To all appearances these larger molecules had an existence which was not explained by the union of components held together by one or several of the various types of chemical bonds. It seemed probable that they resulted from the complete enclosure of one molecule by two or more molecules of another component, in such a manner as to prevent escape unless the strong forces which bound together the enclosing molecules were broken.

Mylius' work has been remarkably verified and extended by Palin and Powell (*2*) who restudied the crystal structures of these and other quinol complex compounds. They found that the quinol molecules link together through hydrogen bonds to form infinite three-dimensional complexes of trigonal symmetry and that these giant molecules may enclose a second component. The several characteristics which compounds of this type have in common led Powell (*3*) to group them together. He observed the firmness with which they were held together though their components appeared to have no strong attractive forces between them; rather, they were held by the enclosure of one by the other, of both by each other, or by some other uncommon mechanism. Because of this unusual type of binding Powell proposed that they be called "clathrate" compounds, from the Latin word *clathratus* meaning enclosed or protected by cross bars of a grating.

Obviously considerations of size and of type of bonding within the cagelike portion of the molecule enter into an understanding of the nature of these compounds. Common sense dictates that the form of such enclosures must contain spaces of size great enough to hold a molecule of the second component. Also, the spaces must be bounded in such a manner as to prohibit escape of the enclosed molecules. When formation is taking place the molecule to be enclosed must be properly orientated when the cage is closing. When a cavity forms without enclosing a molecule of the second component the difficulty of getting one in is equal to that of getting one out. Each of these characteristics has been observed. It has been noted, too, that molecules may and do escape from within the "cages." This process is considered a type of the typical dissociation reaction in which the rate depends upon the energy of activation.

Powell has drawn some generalizations with regard to clathrate compounds (*3*) as a result of careful investigations on specific compounds carried out by him and his colleagues. He and Palin (*4*) have reported a thorough study of the $3C_6H_4(OH)_2 \cdot M$ type compounds in which M may be hydrogen sulfide, sulfur dioxide, hydrogen cyanide, formic acid, hydrogen chloride, hydrogen bromide, or methanol. They made determinations by three-dimensional Fourier methods showing the quinol molecules to be linked together. The giant molecules which result were shown to have forms so open that two such giant molecules could completely interpenetrate each other without having any direct attachments. Within these frameworks the volatile molecules were caught in cavities. Powell refers to compounds of this type as organic, because the framework is organic.

A typical inorganic clathrate compound is that studied by Powell and Rayner (*5*). The framework is inorganic. The compound, $Ni(CN)_2 \cdot NH_3 \cdot M$, is formed by trapping the organic molecule M, where M may be benzene, thiophene, aniline, furan, phenol, or pyrrole. The nickel atoms and the cyanogen groups form sheets from which the ammonia groups project giving alternately planar and octahedral coordination of the nickel atoms. The resulting cavities are too large for ready crystallization but on trapping organic molecules of suitable size crystallization proceeds rapidly. Since size is of such importance here, it has been suggested (*5*) that benzene is readily trapped, but its homologues are too large to be trapped. Therefore the reaction is selective or preferential and crystallization with the formation of $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ may be used as a means of estimating benzene in the presence of its homologues.

In general, the preparation of clathrate compounds appears to be quite simple. For example, crystallization of $3C_6H_4(OH)_2 \cdot SO_2$ is carried out in solutions of quinol in water which have been saturated with SO_2.

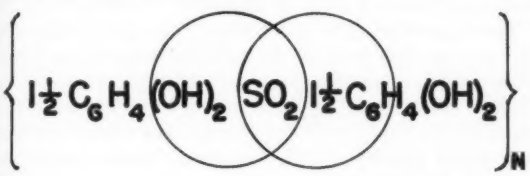
The resulting crystals, like most crystals of clathrate compounds, are very stable under ordinary conditions of storage and do not even give off the odor of the volatile component. They decompose when heated near their melting points, when dissolved in water or when ground in a mortar (*4*).

While each individual compound is most adequately described separately, a general picture may be given by a more convenient representation. Powell introduced the encirclement formula as a means of simplification (*3*). Encirclement formulas may be used where C gives the composition of the cage and M that of the enclosed compound. The formula,

shows a simple clathrate molecule. The formula,

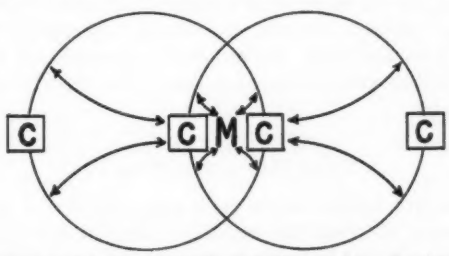
indicates an infinitely extended complex in a crystal. The formula of any clathrate compound is determined by the ratio of available cavities to the amount of cage material.

Using the encirclement formula the compound, $3C_6H_4(OH)_2 \cdot SO_2$, may be written:



The interlocked rings denote mutual enclosure of two identical cageworks. The subscript N outside the brackets shows that the cages are infinitely extended and that there is multiple enclosure of each cagework by the other. The resulting unoccupied space is filled by the inorganic molecule, SO_2.

To explain the restrictions of the SO_2 molecule within the cage Powell employed the following diagram (*3*):



Hydrogen bonds (arrows) hold the molecules together. Covalences preserve the shape and size of the molecules as the cage component and limit the positions and possible directions of the H-bonds.

According to this representation the enclosed molecule, M, could escape by pushing apart the two independent portions of its cage, against their van der Waals attraction. Although this may be a large force, nevertheless if an attempt is made to enlarge the holes of exit the cages will necessarily be brought together more closely elsewhere. Larger repulsion forces will result and prevent enlargements of the exits. The effectiveness of these forces is contingent upon the stability of both the H-bonds and the covalent linkages.

The general encirclement formula,

may be applied to all clathrate compounds. In the formula NM there may be:

(1) A whole number, N, of molecules of component M.

(2) Any fractional amounts of two or more enclosed molecules that add up to a whole number.

(3) Fractional amounts, as in (2), with the qualification that one of the enclosed molecules must be present in some minimum proportions needed to trap the other enclosed components.

(4) Fractional amounts that do not add up to a whole number. This situation may occur when some of the cavities are unoccupied.

Volume alone, not chemical nature, determines the type of molecule, M, to be enclosed. The lower and upper limits of the size of M are governed by the size of the cavities and the sizes of the available exits in the framework. Physical methods are used to make the final decisions in assigning compounds to the clathrate group. However, preliminary assignments may be made as a result of investigations as to properties, molecular ratios, relative volumes of components, and the behavior of homologous or related substances.

Further knowledge of clathrate compounds, and an extension of investigations in this field, may well produce answers to problems which have proved baffling in the past. Certainly the idea of chemical compounds composed of two or more molecules, each capable of separate existence and having no obvious means of chemical union, would not have been predicted. The usefulness of this information has already been demonstrated (*6*). The substance formerly called β-quinol, a supposedly polymorphic form of quinol obtained by crystallization from methanol, has proved to be the clathrate compound $3C_6H_4(OH)_2 \cdot CH_3OH$. Unexpected analytical data may at times be directly traceable to clathrate compound formation from a compound and its crystallization medium. The association of two substances without the necessity of chemical combination in the usual sense of the term may be common in nature. Such compounds may be important in biological systems. The specificity and selectivity of the clathrate formations may serve as a key to complex molecular arrangements in living materials.

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INTRODUCTORY LECTURE IN PHYSICAL CHEMISTRY

LATIMER R. EVANS
New Mexico College of Agriculture and Mechanic Arts, State College, New Mexico

IT IS the unfortunate opinion of many beginning physical chemistry students that they are being confronted with a hodgepodge of unrelated, highly theoretical material. This impression tends to increase the difficulty which most students have in understanding the subject matter of a typical undergraduate physical chemistry course. In an article on the subject of teaching physical chemistry,[1] Kieffer stated that "the greatest challenge to the professor of physical chemistry is to establish a solid relationship in the student's mind between the abstractions themselves and the phenomena upon which they are based."

This objective may be achieved, at least partially, if the course is designed to emphasize the continuity and usefulness of the topics to be covered. The purpose of this paper is to present an idea aimed at the accomplishment of this purpose.

There are admittedly several difficulties which hamper some students in acquiring an understanding of the material in physical chemistry. Some of the impediments to learning which are offered as reasons or excuses by students are the mathematics involved, the lack of adequate preparation in other chemistry or physics courses, and the difficulty of the course itself. Some instructors also feel that inadequate mathematical background is the principal barrier.[2]

It is the opinion of the author, however, that perhaps the major obstacle which prevents students from understanding the material is simply a lack of enthusiasm for the subject. There is some accord with this opinion as evidenced by the number of articles on lecture demonstrations which serve principally to increase interest by augmenting the written and the spoken word with a visual observation and thus simplify the learning process. Also, a recent article indicates that the salesmanship of the instructor is of prime importance.[3]

The suggestion offered in this paper is another device to arouse more enthusiasm for the course in the minds of the students. Furthermore, it is suggested that the fostering of this interest be initiated at the first lecture. It is the author's opinion that enthusiasm will increase if the student can be made to appreciate the importance and significance of each of the topics covered.

The suggested approach toward this aim is simply to devote a portion or all of the initial lecture to a study of some simple chemical process. By this method the student is impressed at the outset by the importance of many of the topics to be covered. He readily realizes how many questions which naturally arise concerning a simple chemical reaction may be answered by a knowledge of the fundamentals of physical chemistry. His interest in the course material is thus heightened from the beginning. Although only a few of the many topics to be covered are introduced in this way, once the student is convinced of the importance of these few, he is more willing to accept the instructor's assurance that all of the material is valuable.

One good reaction for this purpose is the Haber process for the fixation of nitrogen. To illustrate still further subjects covered in physical chemistry, it is helpful to add that the product, ammonia, is to be dissolved in water after it is made. The reactions then would be:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
$$NH_3 + H_2O \rightarrow NH_4OH \text{ (aq.)}$$

It is now helpful if the class pretends that it knows nothing at all about this reaction (often not too much of a pretense!) but is going to explore its possibilities by

[1] KIEFFER, W. F., J. CHEM. EDUC., 29, 226 (1952).
[2] WILLIAMS, H. B., *ibid.*, p. 77.
[3] SCHWENCK, J. R., *ibid.*, p. 368.

doing some research with the eventual plan to erect a plant to market aqueous ammonia. In this case some of the questions which naturally arise and which can be answered by physical chemistry are as follows:

(1) Is it plausible to expect the reaction to occur?

Thermodynamics shows that the change in free energy for this reaction is −3.94 kg.-cal./mol of NH_3 and so it should proceed. Thermodynamics tells us that it is plausible from an energy standpoint but it does not tell us how to make the reaction go.

(2) How much NH_3 will a mol of N_2 give?

The equilibrium constant for this reaction at a given temperature and pressure shows exactly how much NH_3 is in equilibrium with any given amounts of N_2 and H_2. As a corollary to this, it might be mentioned that the specific effects of changes in temperature and/or pressure can be calculated.

(3) How long will be required for the reactants to produce the equilibrium concentration of NH_3?

A study of chemical kinetics in physical chemistry will show how these velocity constants may be determined and how they may be used to determine the length of time required for any given portion of the reactants to be consumed. These constants may also show the effects which altering the stoichiometric ratio of reactants may have on the rate of reaction. Furthermore, the role of catalysts, which alter the rate of chemical reactions, will be discussed.

(4) Since they are gases, how may the quantities of the various materials be readily determined?

The simple gas laws or compressibility diagrams allow the amounts of gases, even up to moderately high pressures and down to reasonably low temperatures, to be calculated from a knowledge of the volume, temperature, and pressure or the critical constants.

(5) Will the reaction be exothermic or endothermic?

Methods for determining not only whether the reaction will absorb or evolve heat but how much heat will be discussed when the subject of thermochemistry is covered. Also the change in the amount of heat absorbed with a change in temperature may be determined.

(6) How much work will be required to heat the reactants to the optimum temperature and to compress them to the optimum pressure?

In the basic study of chemical thermodynamics, the student will learn to handle expressions for the heat capacities of gases and to determine the work and heat involved in isothermal and adiabatic compressions or expansions of gases.

(7) What will be the heat effects when NH_3 is dissolved in H_2O?

Heats of solution and solubilities are not so well understood as some other physical and chemical phenomena, but methods of calculating and handling integral and differential heats of solution will be discussed. Also, based on molecular structure, which is studied in physical chemistry, intelligent guesses concerning solubilities may sometimes be made. For example, NH_3, with an unshared pair of electrons on a reasonably electronegative element, would be expected to be quite soluble in water, owing to the formation of H-bonds, and to evolve heat upon solution.

(8) Will there be storage problems? How basic are solutions of NH_4OH?

The discussion of ionic equilibria teaches the student to calculate readily the pH of aqueous solutions of any reasonable strength. Conductance measurements of aqueous solutions permit ready determination of the degree of dissociation and thus the ionization constant.

(9) What are the possibilities of loss due to evaporation during handling?

Means of determining the vapor pressure of a liquid or the partial pressures of components of a solution at various temperatures or pressures will be studied.

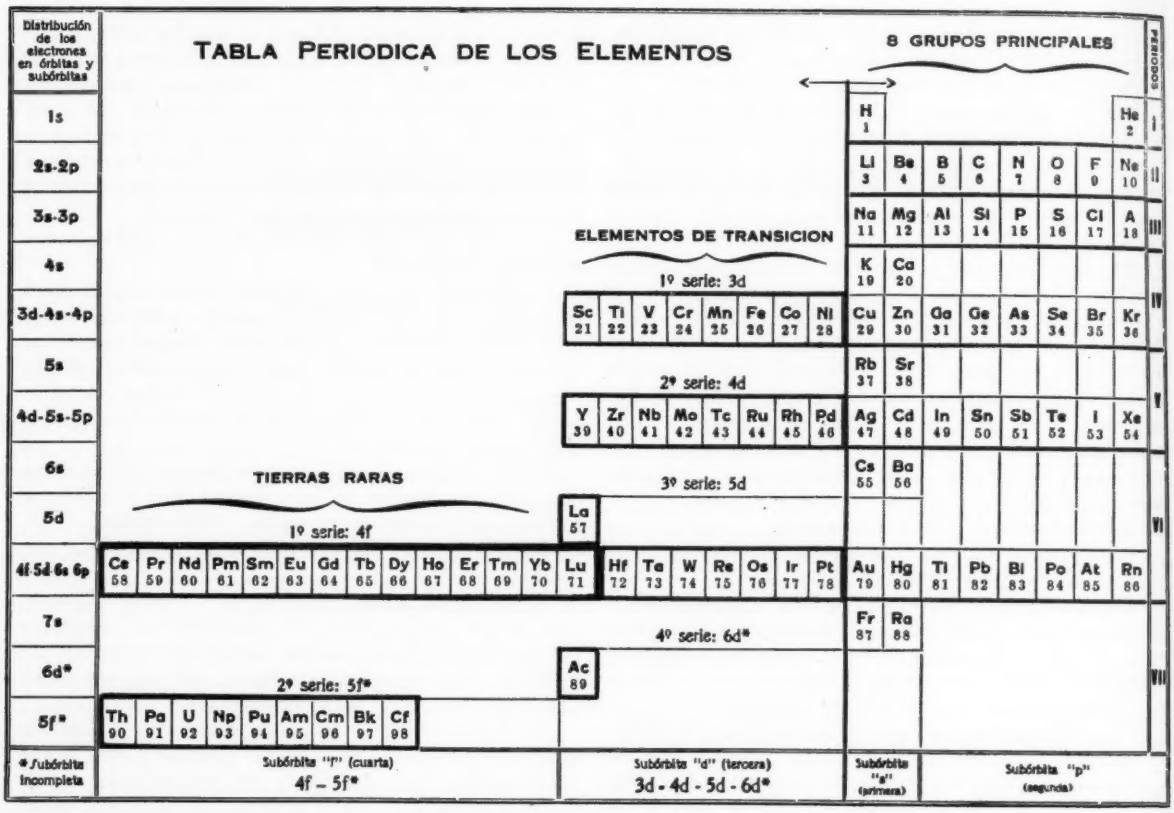
(10) Will there be any difficulties in handling the liquid product?

The physical properties of liquids, such as viscosity and surface tension and their variation with temperature, will be discussed. These and other properties are useful in connection with pumping, pouring, and other handling operations with the product.

All of these concepts are sufficiently simple that the student of elementary physical chemistry can grasp their significance, and there are undoubtedly many other points which can be made to illustrate still other topics which are to be covered in the course. The student is thus able to visualize the value of physical chemistry before starting the course and possibly his interest in the subject matter is stimulated from the beginning. It might also be helpful in pointing out the value of certain sections as they are taken up in the course to refer occasionally to this introductory lecture to refresh the student's memory.

THE PERIODIC TABLE OF ELEMENTS

GIL CHAVERRI R.
Ministerio de Agricultura, San José, Costa Rica



THE purpose of any periodic table is to arrange the elements according to some pattern so that elements that are similar in their properties are grouped or linked together, so as to make them easily distinguishable.

In the accompanying arrangement the elements are divided into three categories, namely: (1) *Regular Elements*, which constitute eight principal groups, (2) *Transition Elements*, which constitute three series plus a unique element of a supposedly fourth series, and (3) *Rare Earths*, divided into two series.

Regular Elements show similarities with one another along *"columns"* (vertical lines) whereas Transition Elements and particularly Rare Earths show similarities along *"rows"* (horizontal lines). This feature is taken care of by placing the Transition Elements and the Rare Earths in specific positions so that each element follows consecutively in order and yet does not intercept the principal groups nor needs to be placed in some unrelated position in the table.

The electronic configurations of the elements constitute the fundamental criterion for the accompanying arrangement. In comparing the distribution of electrons of any one element with that of the next element, a new *"differentiating"* electron is always found, on the location of which this pattern is based.

(1) As far as Regular Elements are concerned, the first column of elements, hydrogen, lithium, sodium, etc., possess one differentiating outermost electron in an *s* subshell. The elements beryllium, magnesium, etc., which constitute the second column, have two outermost electrons in an *s* subshell. (The noble gas helium with no *p* electrons, has been grouped with other noble gases.) Note that:

(*a*) Potassium and copper have *one* and calcium and zinc have *two 4s* electrons, which accounts for placing copper and zinc in the same groups as potassium and calcium, respectively. However, potassium and calcium have *no* electrons in the *3d* subshell whereas copper and zinc each has the maximum number of ten *3d* electrons.

(*b*) Similarly, rubidium and silver have *one* and strontium and cadmium have *two 5s* electrons, which also accounts for grouping rubidium and silver in the first column and strontium and cadmium in the second column. On the other hand, rubidium and strontium have no *4d* electrons at all, whereas in silver and cadmium the *4d* subshell is completely saturated with 10 electrons.

(*c*) Lastly, cesium and gold have *one* and barium and mercury have *two 6s* electrons and are correspondingly located in the first and second columns, but cesium and barium have neither *5d* nor *4f* electrons, while in gold and mercury these subshells are saturated with 10 and 14 electrons, respectively.

(2) The different Transition Series consist of elements that fill up a *d* subshell. In the first Series, elements from scandium to nickel progressively fill the *3d* subshell. With respect to the second and third Transition Series the *4d* and *5d* subshells are, respectively, filled and, finally, there is only one *6d* electron corresponding to the only element of a supposedly fourth Transition Series.

(3) The filling of the *5d* subshell is interrupted after the first electron is located in it. In fact, a second electron is not present in that subshell until the *4f* subshell has been saturated with 14 electrons. This gives rise to the first Rare Earth Series which is accordingly situated between the first and second elements of the third Transition Series. In lanthanum the differentiating electron is the only electron located in the *5d* subshell. In cerium, however, the differentiating electron is located in the *4f* subshell and, for that matter, the elements from cerium to lutetium (14 in number) progressively saturate the *4f* subshell. In hafnium the differentiating electron is again to be found in the *5d* subshell.

(4) In actinium the differentiating electron is located in the *6d* subshell, but in the nine elements that follow, thorium to californium, the differentiating electrons are to be found in the *5f* subshell, which gives rise to the second Rare Earth Series.

The predominant criterion for defining either a Regular Element, a Transition Element, or a Rare Earth is thus the particular location of the differentiating electron. In some cases uncertainty arises; copper, with *ten 3d* electrons and *one 4s* electron is considered here a Regular Element rather than a Transition Element. Divalent copper, with *nine 3d* electrons, shares some of the properties of the Transition Elements, which is not true of monovalent copper, with its *ten 3d* electrons. Also, lanthanum should not be included with the Rare Earths, since it has no *4f* electrons. The same is true of actinium with no *5f* electrons.

The four pairs of elements, potassium and calcium, rubidium and strontium, cesium and barium, and francium and radium, behave abnormally as far as the electronic structure is concerned, in that they possess electrons in external shells while some of the internal subshells are completely empty. Each pair of elements forms by itself a short two-element row in the fourth, fifth, sixth, and seventh periods.

The vertical column at the left of the table gives the order in which the different subshells are being filled up, and together with the line at the bottom of the table will permit one to obtain the electronic configuration of any element, except in the case of a few like chromium, palladium, and iridium which deviate somewhat from the general plan of electronic distribution in shells and subshells.

Other advantages of the table are:

(1) Each particular element, whether a Rare Earth or not, occupies a single place corresponding to its chemical individuality.

(2) The eight principal groups constitute a single block of eight *vertical* columns. In this case, the important historical feature of having vertical columns consist of similar elements is still maintained. Neither slanted, intercepting tie-lines nor other devices to point out similarities among elements are required.

(3) Progressive similarities of the elements in both the columns (groups) and the rows (series) can be pointed out easily.

(4) In the fourth, fifth, and sixth periods, which have more than eight elements, the fact is shown that the first two and the last eight elements of each period are the only elements whose properties are similar to those of the eight elements of the second and third periods.

Note: The table can be further clarified by adopting the familiar concept of A and B families in the case of the first two groups (columns).

A CONSTANT-TEMPERATURE HEATER

S. HORWOOD TUCKER
The University, Glasgow, Scotland

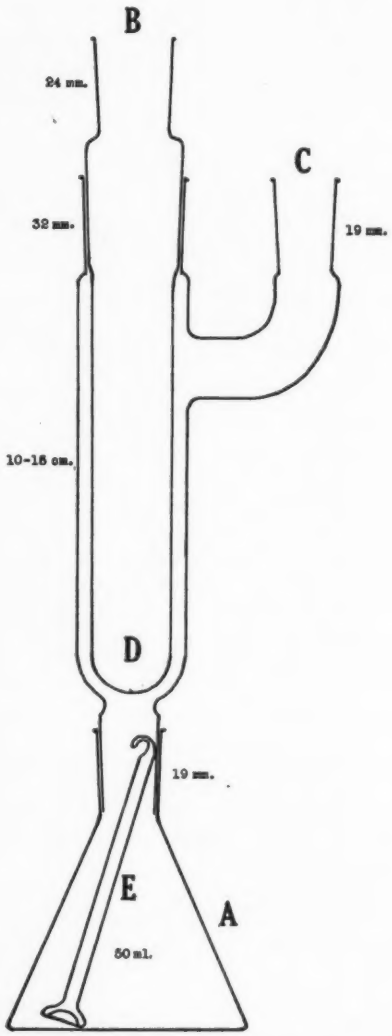
In work on the Ullmann reaction, difficulty was experienced in maintaining reaction mixtures at a constant temperature of 200°, 220°, or 240°, over periods of several hours. Oil baths are messy, and they, as well as metal baths, render it difficult to observe what is proceeding in the reaction mixture: furthermore, the temperature cannot be kept constant. These drawbacks have been overcome by use of the apparatus diagrammed. A liquid of the desired boiling point is boiled in the 50-ml. conical (or spherical) flask, *A*. The burner under *A* is adjusted so that the vapor of the liquid jackets the inner reaction tube, *BD*, but does not enter the side arm, *C*, of the jacketing tube; however, as a precaution, the side arm has an air condenser attached at *C*. The reaction mixture, at *D*, is stirred (thermometer removed) by means of a spiral of tantalum wire attached by rubber tubing to the motor spindle. Boiling of the liquid in *A* is kept regular by use of a bubbler, *E*.[1] Different flasks (*A*) were used for different liquids, and these, when out of use, were stoppered. The same sample was used repeatedly.

Following is a list of readily available liquids which provide convenient heating temperatures above 100°.

Heating-bath Liquids

Approx. temp.	*Liquid* (*b. p.*)
130°	Chlorobenzene (132–3°)
150°	Cumene (isopropylbenzene) (152–3°), bromobenzene (155°)
175°	*p*-Cymene (176°)
180°	*o*-Dichlorobenzene (180°), aniline (184°)
190°	Decalin (*cis* + *trans*) (185–195°), monomethyl diethylene glycol (193°)
200°	Ethylene glycol (200°), methyl benzoate (200°)
205°	Tetralin (207°)
210°	Nitrobenzene (210°), ethyl benzoate (212°), 1,2,4-trichlorobenzene (213°)
215°	Isopropyl benzoate (218°), naphthalene (217°)
220°	Methyl salicylate (223°)
230°	*n*-Propyl benzoate (231°), monobutyl diethylene glycol (231°)
240°	Diethylene glycol (244°)
250°	*n*-Butyl benzoate (250°)
255°	Diphenyl (255°)
260°	Isoamyl benzoate (262°), diphenyl ether (259°)
280°	Dimethyl phthalate (282°)
295°	Diethyl phthalate (296°)
300°	Diphenylamine (302°), benzophenone (305°)
310–5°	Phenyl benzoate (314°), benzyl benzoate (316°)

The above-described apparatus, with a still head fitted at *C*, can function as a Hahn[2] condenser.



The author has also used the simplified version of the above heating apparatus, in which the inner tube, *BD*, is inserted through the middle neck of a 3-necked flask; but this modification has been recently described.[3]

ACKNOWLEDGMENT

My thanks are due to Mr. J. Leslie for constructing the apparatus, and to Mr. J. Findlay for the drawing.

[1] J. Chem. Educ., **26**, 546 (1949).
[2] Hahn, A., *Ber.*, **43**, 420 (1910). See also Arndt, F., *Org. Syntheses*, **20**, 27 (1940); Wilds, A. L., *Org. Reactions*, **2**, 197 (1944).
[3] Linke, W. F., J. Chem. Educ., **29**, 492 (1952).

AN AID TO TEACHING ELECTRONIC THEORY

A. A. HUMFFRAY
Swinburne Technical College, Melbourne, Australia

A STRONG analogy exists between triad tautomerism and the various electronic processes known as the *electomeric effect;* in fact the latter is usually said to occur by the "tautomeric mechanism,"[1] but the author is unaware of any detailed discussion of the analogy.

This paper outlines the method used by the author in presenting the ideas of tautomerism and electronic theory to technical-school students. It utilizes a generalization which may be described as the "X=Y—Z rule," and which may be stated thus:

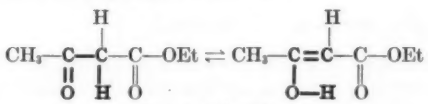
If a molecule contains the grouping X=Y—Z, where X, Y, and Z are elements from Groups IV, V, or VI of the periodic table (Z may also come from Group VII, and X, Y, and Z may be all alike, or different), and if attached to Z there is one of the following:

(*a*) a hydrogen atom
(*b*) an unshared pair of electrons
(*c*) a single unshared electron
(*d*) a positive charge

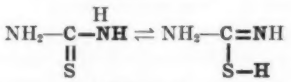
then it may be expected that the "substituent" on Z (*a*, *b*, *c*, or *d*) will have a tendency to move reversibly to X, with bond rearrangement to X—Y=Z, as shown below in detail for each case.

CASE (*a*): X=Y—Z—H ⇌ H—X—Y=Z

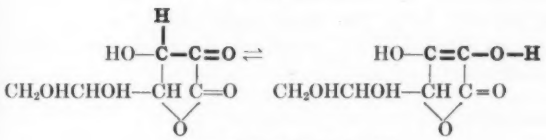
This is the normal case of triad prototropy.[2] A few examples are given, the X=Y—Z—H grouping being shown in boldface type for clarity.



Acetoacetic ester



Thiourea

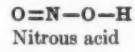


Vitamin C (ascorbic acid)

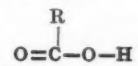
Another characteristic of this system is acidity of the hydrogen (salt formation with metals or metal hydroxides), or at least greater reactivity of the hydrogen than is shown by a hydrogen not so situated.

Examples

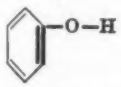
(1) Acidic hydrogen



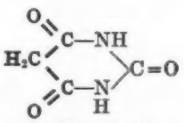
Nitrous acid



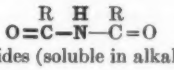
Carboxylic acids



Phenols

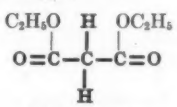


Barbituric acid

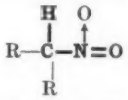


Imides (soluble in alkali)

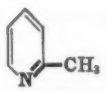
(2) Reactive hydrogen



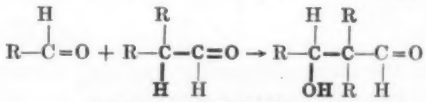
Malonic ester



Nitroparaffins (primary and secondary)



α-Picoline



Aldehydes (aldol condensation)

The student is first introduced to the X=Y—Z rule in connection with the greater acidity of acids and phenols compared to alcohols. Thereafter little difficulty is experienced in recognizing the grouping when present in a new compound, and the student readily appreciates the reactivity of the hydrogen atoms in examples (2) above.

Cases (*b*), (*c*), and (*d*) constitute the three possible types of electronic rearrangement considered in the usual "valence bond" treatment of resonance, when writing down "canonical forms" of a structure. (The purely hypothetical nature of "canonical forms" is

[1] REMICK, A. E., "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York, **1947**, p. 62.
[2] GILMAN, H., Editor, "Organic Chemistry," 2nd ed., John Wiley & Sons, Inc., New York, **1947**, p. 1937.

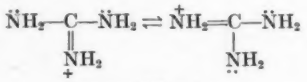
stressed in this treatment as usual.) These cases are discussed only after the student has become quite familiar with the application of the X=Y—Z rule to tautomerism.

CASE (*b*): X=Y—Z: ⇌ :⁻X—Y=Z⁺

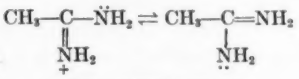
It must be noted here that X always *gains* one negative charge and Z always *loses* one negative charge, while the polarity of Y is unchanged. This is first stated dogmatically, but is easily verified from a consideration of the number of electrons associated with each atom in each of the above structures. (*Note:* X may be positive originally, or Z may be negative.)

Examples

(1) Positively charged X

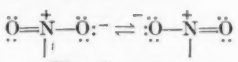


The guanidine ion

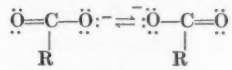


The acetamidine ion

(2) Negatively charged Z

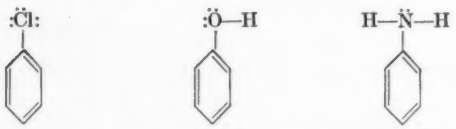


The nitro group



The carboxylate ion

(3) X and Z uncharged. Examples are benzene derivatives such as:



in which the atom attached to the ring possesses an unshared pair of electrons. Thus:

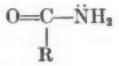
A repetition of the process, going around the ring, gives

and, similarly,

This example shows that no negative charge is possible on the meta carbon atoms. The discussion of orientation in aromatic substitution is one of the most useful applications of the X=Y—Z rule, being more easily grasped by students than the usual "curved arrow" method of indicating electron shifts.

It may be noted here that the unshared pair of electrons has a lower reactivity than usual (*i. e.*, a smaller tendency to form coordinate bonds), as is shown by the weaker basic strength of aniline

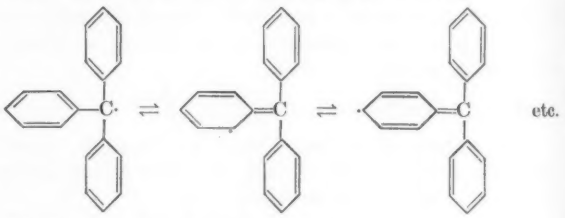
and of amides



compared to aliphatic amines.

CASE (*c*): X=Y—Z· ⇌ ·X—Y=Z

The commonest example is provided by the stable aromatic free radicals, *e. g.*, triphenylmethyl

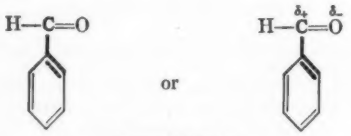


CASE (*d*): X=Y—Z⁺ ⇌ ⁺X—Y=Z

In this case X gains one positive charge, and Z loses one positive charge; again this is easily verified by considering the number of electrons associated with each atom in each of the "canonical forms."

This case should be preceded by a discussion of the relative electronegativities[3] of the elements; this is usually done in connection with the discussion of dipole moments and the inductive effect. (For any period of the periodic table, the electronegativity of an element, *i. e.*, its attraction for electrons, increases with atomic number.)

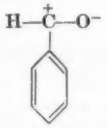
Examples



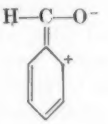
Benzaldehyde

[3] REMICK, A. E., *op. cit.*, pp. 26, 144.

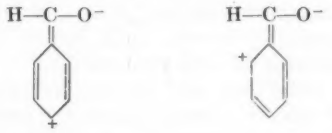
Here the carbon atom attached to the ring possesses no unshared electrons, but is linked to an oxygen atom, which has a greater electronegativity; therefore the carbonyl group is polarized as shown above. If complete polarization of the carbonyl group is assumed to occur (on the demand of the attacking reagent), giving the "structure"



the positive charge on the carbon can then move as postulated above, producing

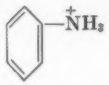


and, by a repetition of the process, the following:

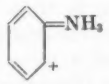


The other meta directing groups, R--C=O, COOH, NO_2, CN, etc., can be treated similarly.

In all instances the application of the X=Y—Z rule is not permitted to negate the "octet rule," *e. g.*, the anilinium ion,



possesses the X=Y—Z^+ structure, but obviously cannot rearrange to



etc.

without giving the nitrogen ten shared electrons.

It should be noted that tautomerism, as discussed in case (*a*), can be treated as a combination of case (*b*) or (*d*) plus movement of an ion to follow the negative or positive charge, respectively.[4]

The examples given in this paper are illustrative of a method for providing students with a simple entry into electronic theory, based directly on the analogy between it and tautomerism.

ACKNOWLEDGMENT

The author wishes to express his indebtedness to Dr. Francis Lions of Sydney University, who first pointed out the possibilities of the X=Y—Z rule as applied to tautomerism (case (*a*)).

[4] BAKER, J. W., "Tautomerism," D. Van Nostrand Co., New York, 1934.

SUPPORT OF BASIC RESEARCH

TRADITIONALLY, we have looked to the universities for the advancement of knowledge, and we depend upon them largely for all research into the fundamentals of science. To industry falls the task of applying new knowledge to useful ends and of furthering research and development focused on new materials, processes, and products. . . . Government encourages research of all kinds with a view to development of new weapons and supports a variety of investigations in such fields as agriculture and public health. But all this chain of obligations hangs upon fundamental research, and the future vitality of countless enterprises depends upon the soundness of our national effort in this domain. The responsibility for the support of basic science cannot be delegated wholly to the university; it must be shared by industry and government, by business and by the public at large.—Julius A. Stratton, Massachusetts Institute of Technology.

THE REACTIVITY OF SOLIDS[1]

J. ARVID HEDVALL
Chalmers University of Technology, Göteborg, Sweden

WE KNOW that matter exists in three states: solid, liquid, and gaseous. It is a characteristic of the solid state that the atoms are placed so close together that the linking forces prevent them from moving from one position to another. They only oscillate in positions of symmetry characteristic of the substance in question. The interior "architecture" of the crystal build, the so-called lattice, also determines the exterior shape of the crystals.

In liquids or melts, and particularly in gases, the distances between the atoms are so large and the mutual attraction consequently so small that movement can take the form of real migration of the atoms.

Every chemical reaction requires such a transport of matter. Evidently, reactions will therefore occur far easier in liquids and gases than in solids.

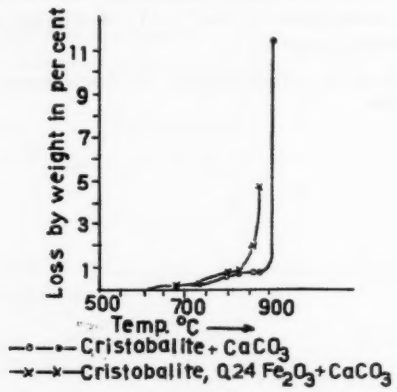


Figure 1

For a long time the chemistry of solids remained a blank spot on the chemical map. Modern investigations, however, showed that the chemical sterility of crystals was overaccentuated.

It is characteristic for almost every solid substance that a change of its crystal lattice takes place at a certain temperature, peculiar to that particular substance. A process such as this is of course impossible without changes in the positions of the atoms. A transport of matter consequently exists in such so-called transition states, which therefore should be favorable for chemical reaction with surrounding media.

This was the working hypothesis of the first experiments to determine if solids in such states of mobility would prove reasonably reactive—perhaps even in mixtures with other solids. If so, it would mean the existence of reactions in powders, reactions that were still unknown or misinterpreted at the beginning of this century. When systematic investigations started (1912) X-rays had not yet shed their light on the shrouded darkness of crystal structure.

The aforementioned idea about the reactivity of solids in transition states involves a simplification of the problem according to modern views, but it proved highly fruitful. In contemporary industrial practice powder reactions play a very important part and are capable of numerous applications. For instance in the manufacture of cement, glass, and porcelain, and in metallurgical processes, such factors influence reactions occurring at high temperatures.

Powder metallurgy and the manufacture of a great number of modern ceramic products (cermets, refractories, spinels, etc.) used for chemical and electrical apparatus, depend on the possibility of sintering or other reactions in the absence of melts or gases.

About 40 years ago the first paper was published establishing the possibility of reactions in powder mixtures of oxides. Pigments, used in ceramic processes, were produced by this method.

Even in these early experiments it was evident that the structure and origin of the starting material seriously influenced the reactivity. A few years after the enigma of X-rays had been solved by Laue, an X-ray investigation of the well-known Swedish Red Pigment showed that the ferric oxide does not attain its full luster unless it is made from iron sulfate. It was shown that such effects depend on small but significant disturbances of the crystal structure which are a kind of hereditary characteristic persisting from the starting material.

Such imperfections are highly interesting even from the technical point of view, as they can be caused or prevented deliberately. The physicochemical behavior of a solid toward surrounding media, whether solid, liquid or gaseous, can consequently be controlled. Abnormal dislocations in the structure of the crystal may influence reactivity.

Changes of this kind are now well known for their widespread practical importance. For one thing, there is the problem of attack by melts on furnace material; the latter must not consist of substances that change their structure at the temperature of the processes in which they are used. On the other hand there is the use of the increased reactivity in such states in order to accelerate reactions in powder mixtures. These reactions are extensively employed in industrial practice.

[1] HEDVALL, J. A., "Reaktionsfähigkeit fester Stoffe," Edward Brothers, Ann Arbor, 1943; "Einführung in die Festkörperchemie," Vieweg u. Sohn, Braunschweig, Germany, 1952.

Compounds of the spinel type between various oxides and their solid solutions are nowadays important substances for production of devices for television, radar, and jet planes.

It has also been demonstrated that even extremely small additions of foreign substances may decisively influence the chemical properties of non-metallic substances. Such influences explain old-established experiences in metallurgical practice, where it is frequently observed that ores of different origin behave quite differently in spite of practically identical composition (see Figure 1).

The changes caused by gases dissolved in solids may by cited in this connection. There are a number of old experiences in metallurgical, ceramic, and glass furnace production concerning the influence of even such kiln atmospheres which cannot participate in chemical reactions. Quartz, ferric oxide, and alumina, for instance, show enormous difference in reactivity and sintering capacity in nitrogen and in oxygen (see Figure 2). The significance of these results for catalytic processes, powder metallurgy, powder ceramic processes, and annealing technique is quite clear.

A phenomenon of considerable economic consequence for the metallurgical industries (*e. g.*, regarding molds for steel castings and furnace bottoms) is the part played by the particle shape and the grain-size distribution with reference to the adherence of melts or stiffening castings. Adherence is, of course, far from desirable, and it is possible to avert it through consideration of the aforementioned factors.

Another discovery is that of a group of so far unknown reaction types—the so-called place-change reactions. These reactions, *e. g.*, between oxides and salts, sulfides, phosphides etc., take place at surprisingly low temperatures.

$$AO + BXO_n \rightarrow AXO_n + BO + Q$$
$$AO + BX \rightarrow AX + BO + Q$$
$$AO + BX + nO_2 \rightarrow AXO_{2n} + BO + Q$$

AO and BO are oxides, AX and BX halides, sulfides, phosphides, carbides, etc., AXO_n and BXO_n are salts of oxygen acids, Q is the development of reaction heat.

Reactions of this type which may occur not only in powders but also between solids and melts, offer a more satisfactory explanation of several well-established metallurgical processes, *e. g.*, the basic Bessemer process. Metallurgical methods for removing carbon, sulfur, phosphorus, silica, and selenium from metals are modern applications.

There are at present several methods for studying changes in the lattice: by X-rays, measurements of electrical conductivity, and by means of radioisotopes, or observation of abrupt changes in the velocity of liberated radioactive gases (the Hahn emanation method).

At a comparatively early date investigations were also made into the electrical conductivity of non-metallic solids. The results gave information about the type and mobility of the particles, and in certain cases also revealed the course of those reactions in the solid state in which the transport of matter is carried out by ions and electrons.

The investigations have shown that the transport of matter may be carried out both by electrically charged

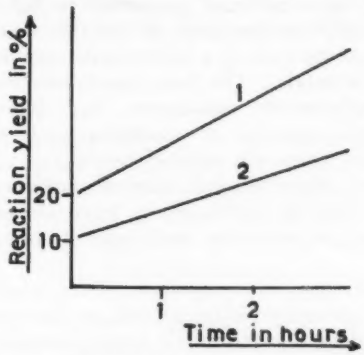


Figure 2. Reactions at 600°C. Between CaO and SiO_2, Preheated in O_2 (1) and in N_2 (2)

atoms (ions) and by atom aggregates or surface molecules. The transport can take place by several routes, either rapidly at the surface or through interior submicroscopic canals, or more slowly through the crystal lattice that has been more or less disturbed (see Figure 3). Quite recently it was possible to verify experimentally the different stages or types of diffusion in a number of cases by means of radiotracers.

Investigations of this type are one of our most pressing tasks. The results are equally important from the point of view of both theory and practice. In modern industry it is impossible to content oneself merely with the knowledge *that* a reaction actually does take place. It is imperative to know also *how and why* and to know the material one is working with.

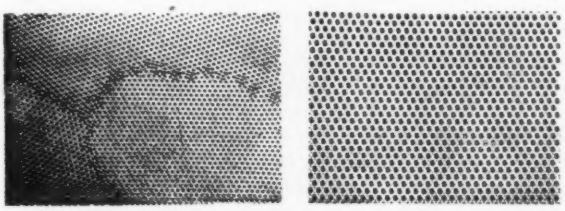


Figure 3. Crystal Lattices (Bubble Models, Bragg) With and Without Imperfections

Our survey would be too incomplete without mentioning a few particularly exciting forays into the long-forbidden territory that was the chemistry of solids.

Chemists had previously varied only the temperature in order to influence the transport of matter. It was found, however, that changes in the magnetic and electric states of the solids could also result in surprisingly large changes of reactivity. From the point of view of theory it may be said that entirely new realms of research were opened. The conceptions of magnetochemistry and electrochemistry have been enlarged.

The results are already being used in certain branches of the metallurgical industry, catalytic processes, and electrotechniques.

At about the same time it was shown that all substances, not only those generally treated in photochemistry, have different properties in light and in darkness, and the discovery of this fact was another milestone on the road to a better understanding of the chemistry of solids. The first experiments were made with phosphorescent substances, and demonstrated their altered capacity of adsorbing such things as organic dyes when in a state of irradiation. The door to this new photochemical research darkroom is still only ajar, but the early results have already found applications in television and radar techniques (see Figure 4).

The new types of magnetochemistry, electrochemistry, and photochemistry, as well as the marked influence of deviations from the normal composition on the adsorption capacity of a substance, are new and fascinating fields of theoretical and technical research.

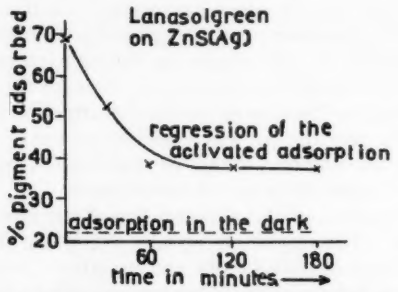


Figure 4. Regression of the Photo-activated Adsorption

The effect of supersonic waves has also been studied, particularly with reference to the tarnishing of metals in reactive gases. An accelerated formation of surface coatings and more even distribution was established in the case of oxide layers (see Figure 5). This can be exploited technically for procuring thin, insulating layers between the metal sheets in transformers.

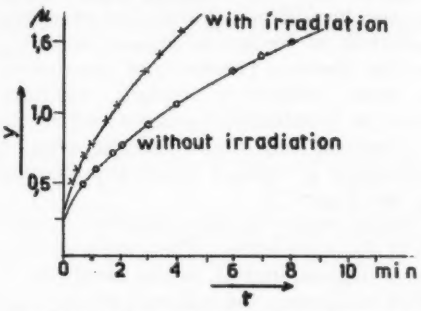


Figure 5. Tarnishing of Copper in Iodine With and Without Supersonic Irradiation

The possibility of altering, within wide limits, the behavior of solid substances towards surrounding media—solids, liquids, or gases—is nowadays an established fact—a fact which has grown into a highly important factor industrially as well as theoretically.

Organic and medical chemistry will find applications in the fields of high-molecular substances. Organic substances have often very marked transition intervals, with consequently enhanced vulnerability or increased polymerization velocity, a fact which cannot leave the textile and plastics industries unmoved.

We have now made a short trip through the hillocky terrain of this new domain of chemistry, pausing at some observation posts. The observation posts have been selected for the instructive view obtainable over both theory and applications. Every kind of industrial production is dependent on the behavior of solid substances toward surrounding media. Intimate collaboration between theoretical research and industrial application is a necessity, still not always accepted, for continued progress.

One of the latest synthetic products to be developed is "synthetic" gravel. The ingredients are soil, inexpensive chemicals, and sulfite liquor. The "gravel" is made in briquetting machines and offers promise for solving road building problems where natural gravel is scarce.

A SCIENCE CLASS INVESTIGATES AN ADVERTISEMENT

HAYM KRUGLAK
University of Minnesota, Minneapolis, Minnesota

One of the perennial problems in education is to make science meaningful to the student in terms of his everyday experiences. This problem is particularly difficult in the case of a general education course for non-science majors. During the past few years the number of science courses for general education increased rapidly. These courses propose to give a broad understanding of the aims and methods of science, to illustrate the application of science to daily living, and to provide practice in scientific thinking. Although there is a diversity of educational philosophies and methods in science teaching (*1*), two objectives appear to be common to practically all programs of general education: (*a*) the understanding of the scientific method and the ability to use it; (*b*) the development of scientific attitudes and practice in their use.

I challenged elsewhere (*2*) the operational validity of the so-called "steps" of the scientific method. I tried to bring out that (*a*) these steps could not be applied as a magic formula, (*b*) the evolving nature of science points to dynamic characteristics of its methods, (*c*) there were probably many methods of inquiry, and (*d*) there was no satisfactory all-inclusive definition to date. It has been my intention to stress the pedagogical sterility which resulted from the oversimplification of what appears to be a highly complex series of processes.

No one can survey the tremendous mushrooming of the sciences without realizing that there must be something, some constellation of abilities, attitudes, and experiences which have been responsible for this growth. Now, one cannot quarrel with a logically constructed definition of the scientific method, but the real difficulty arises when one attempts to bring such a definition into a sharp operational focus in the classroom. To devise situations which will give the student "the point of view with which a scientist approaches his problems" (*3*), is a task which challenges the most able and experienced science teacher.

It has been said that the average American does not understand science, but believes in it. Some advertising men are keen enough psychologists to recognize and exploit the public's faith in the objectivity of science and the integrity of scientists. In recent years there has been a veritable deluge of advertisements in which "science" and "scientists" are used to lend validity to the claimed superiority of the advertised product. Typical statements are: "Science discovers new easy way. . ."; "Science proves. . ."; "New evidence proves . . ."; "...First to give you scientific facts in support. . ."; "An achievement of Science..."; "These scientifically controlled tests revealed..."; "Famous independent laboratory proves. . . ." An examination of the so-called "evidence," "facts," or "tests" reveals either an appalling ignorance of science on the part of the advertising writer, or a most cynical attitude that often borders on the fraudulent.

Many advertisements suggest "tests" to be carried out by the consumer. More often than not such "tests" are strongly biased and provide a perfect example of how *not* to carry out a scientific investigation. I have found that some of these advertisements can be used effectively to teach the methodology of scientific research (*4*). With appropriate guidance, the "test" can be developed by a science class into a research project that illustrates scientific methods and attitudes. The students' activities include a critical reading of the advertisement, an analysis of the evidence presented in it, planning an experimental design for verifying the advertiser's claim, collection and organization of data, drawing conclusions from the empirical results, and the recognition of their limitations.

THE VEL "HAND-HEAT" TEST

The manufacturers of the detergent Vel claim that its users will suffer "no detergent burn to hands." Newspaper advertisements and television commercials give directions for a "prove-it-yourself" test. To people with little background in science, the test appears to be reasonable; it is simple and quick; the consumer collects the data and makes the comparison with another detergent; a plausible explanation of the difference in heat feeling is provided by the use of the statement: "*Vel contains no irritating alkalies.*" However, a person with the most limited training in scientific methodology would quickly recognize the glaring defects of the "test" procedure. The Vel advertisement seemed to me an ideal instructional device for testing the ability of students "to read and evaluate new articles and popular writing on scientific developments" (*3*), for relating classwork to a practical consumer problem, and for practice in the "ability to apply science knowledge to new problems and situations" (*3*).

The Natural Science 5 class, consisting primarily of non-science majors in the arts college, completed the textbook chapters on Ionic Reactions, Acids, Bases, and Salts, and Chemical Energy (*5*). The class discussion was based on the questions at the end of the chapters, collateral reading (*6*), and lecture demonstrations. The electrical conductivity in electrolytic and nonelectro-

lytic liquids, the electrolysis of copper bromide, common indicators, titration, reactions of silver ion with chloride ion solutions, and a few typical exothermic and endothermic reactions were demonstrated. In the laboratory the students tested a number of solutions by means of indicators, neutralized a sodium hydroxide solution with hydrochloric acid, titrated household vinegar, and computed its normality and percentage of acetic acid.

When I was satisfied that the students had a fair understanding of the rudiments of the ionization theory, I read the Vel advertisement to the class. Most of the students had read the advertisement in the newspapers, or seen the commercial on television. The following questions were then proposed: Is the Vel hand-heat test a satisfactory method for testing "detergent burn"? Are there any serious shortcomings in the test, and if so, what are they? Is the evidence presented relevant to the hypothesis under investigation? If you have objections to the Vel test procedure, how would you revise it?

The merits and the deficiencies of the Vel test were discussed and a modified experimental procedure was developed. Motivation was at a very high level, and the students did not have to be prodded to offer criticisms and suggestions. The instructor acted as a moderator, now and then injecting additional questions and comments so as to clarify the meaning of such concepts as: hypothesis, experimental facts, objective evidence, observation, judgment, experimental bias, randomization, experimental error, etc. It was agreed that the Vel "hand-heat test" had some good features: (*a*) the consumer was urged to verify by actual trial the effect claimed in the advertisement; (*b*) the directions given for the test were simple and direct; (*c*) the reader was given the choice of the second detergent; (*d*) the explanation of the observed effect appeared to be consistent with known facts about alkalies. The most serious objections to the test were: (*a*) the effect on the observer's judgment caused by the knowledge of the results *before* the performance of the test; (*b*) the difference in the method of handling the detergents during the test and in home use; (*c*) the probability of always placing the control detergent in the left hand, as shown in the pictures illustrating the test.

Upon suggestion from the instructor the class was willing to design and carry out an investigation that would tend to eliminate the obvious systematic errors of the Vel test.

The factors to be investigated were discussed: sex differences, left-right hand sensitivity, day-to-day consistency of subject judgment on same detergents, heat effect from several detergents, day-to-day consistency of subject's judgment on different detergents. The discussion of controls brought up a number of questions: How much detergent should be used? What should be the temperature of the water? How long a time should the detergents be allowed to be in contact with the hands? At what time of day should the test be carried out? Before or after washing the hands? Is it important to consider the surface temperature of the hands, particularly if one has just come in from the outdoors? Should the test be performed with the hands open, as shown in the advertisement, or should the hands be closed as demonstrated on television? How should the control detergents be selected, and how many of them be used? How much time should elapse between each comparison?

The matter of keeping uniform records of the observations was brought up and settled. Since the test interpretation was a matter of the observer's judgment,

Results of the Vel "Hand-Heat" Test
Natural Science 5, University of Minnesota, March, 1953
(All numbers are per cent of responses. *B* = boys, *G* = girls, *T* = total)

	Test 1 left: Vel right: Vel			Test 2 left: Vel right: Breeze			Test 3 left: Vel right: Dreft			Test 4 left: Dreft right: Dreft			Test 5 left: Vel right: Dreft			Test 6 left: Dreft right: Vel			Test 7 left: Dreft right: Breeze			Test 8 left: Breeze right: Vel		
I. HANDS OPEN (Boys: $N = 23$; Girls: $N = 16$)																								
(*a*) *In which hand(s) was heat felt?*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*
Left	17	31	23	4	6	5	26	13	21	9	6	8	35	19	28	13	6	10	22	6	15	48	44	46
Right	9	13	10	35	25	31	0	13	5	17	0	10	4	13	8	39	13	28	56	25	44	0	0	0
Both	35	13	26	31	31	31	35	19	28	9	25	15	13	6	10	13	19	15	4	19	10	17	13	15
Neither	39	44	41	31	37	33	39	56	46	65	69	67	48	63	54	35	63	46	17	50	31	35	44	39
(*b*) *Which hand felt most heat?*																								
Left	17	37	26	13	13	13	43	31	38	4	13	8	48	31	41	9	6	8	22	19	21	56	50	54
Right	26	19	23	52	31	44	9	13	10	17	6	13	4	6	5	43	25	36	61	31	49	0	6	3
No difference	56	44	51	35	56	44	48	56	51	78	81	79	48	63	54	48	69	56	17	50	31	43	44	44
II. HANDS CLOSED (Boys: $N = 23$; Girls: $N = 17$)																								
(*a*) *In which hand(s) was heat felt?*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*	*B*	*G*	*T*
Left	17	12	15	4	6	5	35	47	40	4	24	13	48	47	47	4	6	5	17	6	13	61	35	50
Right	30	12	23	30	24	28	4	12	8	22	12	18	9	6	8	56	24	43	61	53	57	4	0	3
Both	43	47	45	57	53	55	35	35	35	22	24	23	26	24	25	22	47	33	17	24	20	30	65	45
Neither	9	29	18	9	18	13	26	6	18	52	41	48	17	24	20	17	24	20	4	18	10	4	0	3
(*b*) *Which hand felt most heat?*																								
Left	26	35	30	17	24	20	56	65	60	9	29	18	70	59	65	13	24	18	22	6	15	83	82	83
Right	39	24	33	66	41	55	9	12	10	35	12	25	13	18	15	61	53	58	70	82	75	9	6	8
No difference	35	41	38	17	35	25	35	24	30	56	59	58	17	24	20	26	24	25	9	12	10	9	12	10

the criterion for accepting the significance of the difference between the heat sensations was arbitrarily set at 25 per cent of the observers reporting such a difference. There was a unanimous opinion that all the samples to be tested should be coded so that the observer would not know the names of the detergents until after the observations had been made and the conclusions reached.

I went to the supermarket nearest the university campus and made a list of nine available detergents. The names of the detergents were alphabetized and numbered successively. Two detergents could not be used: one was a liquid, and the other was tinted. In addition to Vel, two detergents were selected by the use of a table of random numbers. A tablespoonful of a detergent was placed and sealed into each of 16 envelopes, coded by me for testing order and hand to be used. Each student got a set of envelopes and a sheet summarizing the nature of the test and its design, giving the directions and providing a simplified scheme for recording the observations. The sheet is reproduced below.

(3) Vel *did* produce the sensation of heat at the 25 per cent level of significance agreed upon at the time the experiment was set up.

(4) There were substantial differences in the heat sensations of individuals with a corresponding reduction in the confidence to be attached to the conclusions.

(5) Vel produced more heat sensation than one of the comparison detergents (Dreft) and less than another (Breeze), thus invalidating the claim in the advertisement with respect to one of the two randomly selected detergents.

(6) It was agreed that the above conclusions were subject to the limitations inherent in the small size of the sample population, its characteristics, and the large experimental errors inherent in this particular test situation.

The students were then asked to suggest a more sensitive and conclusive procedure for checking the validity of the Vel hand-heat test. Among the suggestions made and discussed were: the use of a calorimeter, titration of a number of soap and detergent solutions, random selection of a larger population sample, better

UNIVERSITY OF MINNESOTA

Natural Science 5, Winter 1953

HAND-HEAT TEST

1. The purpose of the test is to compare the effect of 3 detergents. The procedure suggested by the manufacturer of one of the detergents will be used.
2. Two of the detergents were selected at random from a list of 7.
3. The 3 detergents were distributed into 16 envelopes according to the following scheme:

	Test number							
Hand	1	2	3	4	5	6	7	8
Left	*a*	*b*	*a*	*a*	*b*	*a*	*c*	*b*
Right	*b*	*a*	*b*	*a*	*b*	*c*	*a*	*c*

4. The tests are to be performed at the rate of two per day: one in the morning and one in the evening. Each envelope contains one tablespoonful of a detergent, but not necessarily in the order given above.
5. *Directions:*
   a. Dip hands in water at room temperature.
   b. Empty the two envelopes for a given test into each hand. It would be best to have someone help you. Close your eyes during the test.
   c. Keep your hands open for about $^1/_2$ minute.
   d. Close your hands firmly for another $^1/_2$ minute.
   e. Record your observations in the following table.

Reaction	*(O) with hands open* *(C) with hands closed*	*Test number* 1	2	3	4	5	6	7	8
Circle hand or hands in which heat was felt.	(O)	L R	L R	L R	L R	L R	L R	L R	L R
	(C)	L R	L R	L R	L R	L R	L R	L R	L R
Circle the hand in which the heat feeling was the greatest.	(O)	L R	L R	L R	L R	L R	L R	L R	L R
	(C)	L R	L R	L R	L R	L R	L R	L R	L R

RESULTS

Of the 45 students in the class, 40 returned the data sheets: 23 boys and 17 girls. The percentage of each type of response was computed and the results tabulated on the blackboard, as shown in the table.

On the basis of the experimental results, the class arrived at the following tentative conclusions for the open-hand test:

(1) There appeared to be no consistent difference between the responses of boys and girls. The hypothesis of no difference could probably be accepted.

(2) The differences in heat sensitivity between the left and right hand were probably not significant for this test.

control of the water temperature, and a number of others. Anticipating the suggestion to determine quantitatively the alkalinity of the detergents, I dissolved 1 g. of each in 100 ml. of distilled water and had the pH determined with an accurate meter. The resulting pH values were recorded on the blackboard: Breeze, 9.80; Vel, 7.05; Dreft, 7.0. Although the students in the class had little or no mathematical background so that the exact definition of pH would not be meaningful to them, the concept of the hydrogen ion concentration was explained qualitatively and exemplified by giving the approximate pH values for a number of substances (7). By comparing the pH of Breeze with that of 0.01 *N* ammonia (10.6), the relatively low

alkalinity of the detergent producing an unmistakable heat sensation was demonstrated.

The over-all conclusion by the class of the Vel hand-heat test was that it did not demonstrate uniquely the superiority of the product. Since the heat of solution is not necessarily related to the concept of "detergent burn," the suggested test was inappropriate for the test of the hypothesis stated in the advertisement. The reaction of the skin may or may not be the cause or the effect of any observed heat. Besides, the detergents tested were not used under normal laundry and kitchen conditions. The actual use of two detergents for equal periods of time, under the same conditions, and the examination of hands before and after the test period would yield more relevant data for the test of the hypothesis that "Vel helps you avoid rough, red hands—causes no 'Detergent Burn.' "

The analysis of the advertisement, the planning of the revised test, and the final discussion took two class periods. The total time spent by the students outside the class collecting their data was of the order of one hour.

EVALUATION OF PROJECT

I believe that the Vel hand-test provided the students with an illustration of a typical pseudo-scientific experiment. The revision of the test procedure, the observation and recording of data, and the drawing of conclusions undoubtedly provided the class with practice in applying scientific knowledge and methodology to an unfamiliar but real situation. I hope that the exercise demonstrated to the students "the understanding of the point of view with which a scientist approaches his problems and of the kinds of things that he does" (*3*). The critical reading of the Vel advertisement was also planned to provide the students with some practice in the "ability to read and evaluate news articles and popular writing on scientific developments" (*3*). I believe that the methodology used by my natural science class paralleled the type of critical analysis in which scientists engage when they read the reports of each other's work.

From observations in class it appeared that most of the students made some sort of a contribution—voluntary or solicited—to the analysis and discussion, the motivation was better than average, and the percentage of returned data sheets was very high. Did the investigation leave the students with a permanent ability to apply scientific methodology and to display the scientific attitude? There are no valid paper-and-pencil tests that would give an answer. The future *behavior* of the students in similar situations will provide the only *real* evaluation of the instructional outcomes.

Of course, not all advertisements distort the "scientific method," or claim a product superiority on the basis of a non-existent principle. Thus, a recently advertised magnesium metal silver detarnisher was a good example of a correctly applied scientific generalization, and was used by me to illustrate the electromotive series. The alert science teacher will find many examples of "right" and "wrong" science in the news and advertising sections of the popular press. The use of such items as sources of classroom discussions and projects provides not only stimulation to teacher but makes science more meaningful to the student as a consumer and enlightened citizen in a democratic society.

ACKNOWLEDGMENT

I am indebted to Professors H. H. Barber of the School of Chemistry and N. M. Hintz of the Department of Physics for constructive criticisms of the manuscript and stimulating discussion. Professor Barber was also kind enough to make the pH determinations of the detergents used in the study.

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Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

Stephen E. Merrill, Brunswick, Maine

FIFTEENTH SUMMER CONFERENCE

THE 15th Summer Conference of the New England Association of Chemistry Teachers was held August 24–29 at Bowdoin College, Brunswick, Maine, with John E. Cavelti, Allegheny College, and Guy F. Burrill, Keene High School, Keene, New Hampshire, as co-chairmen. James S. Coles, recently inaugurated as president of Bowdoin, welcomed the conference most cordially to the Brunswick campus and spoke briefly of difficulties students may expect to encounter in college as the result of a poor selection of preparatory courses in secondary schools. He recommended that promising students be advised early in their school years to elect science courses, and particularly mathematics and foreign languages, to avoid learning too late that they may not elect many preprofessional curricula upon admission to college without making up their deficiencies.

There were 238 teachers and guests enrolled at the conference, of whom about two-thirds were from New England. Besides the New Englanders present, there were 28 from New York, 18 from Pennsylvania, ten from New Jersey, four from Maryland, three from Indiana, two each from Illinois, Ohio, and Wisconsin, and one from both California and Michigan. Besides these there were three from Montreal, Province of Quebec. The following have attended all 15 summer conferences:

Mr. and Mrs. Grover C. Greenwood, Harding High School, Bridgeport, Connecticut.
Mr. and Mrs. S. Walter Hoyt, Boston Technical High School, Boston, Massachusetts (retired).
Mr. Alfred R. Lincoln, Western Massachusetts School of Pharmacy, Willimansett, Massachusetts.
Miss Evelyn L. Murdock, Stonington High School, Stonington, Connecticut.

Miss Elsie S. Scott, Northfield School for Girls, Northfield, Massachusetts.
Dr. John R. Suydam, St. Mark's School, Southboro, Massachusetts (retired).
Mr. Elbert C. Weaver, Phillips Academy, Andover, Massachusetts.

In addition to the program of addresses by speakers from colleges and chemical companies, several round tables were held under the leadership of four members of the conference: "Ionic Theory," William B. Meldrum, Haverford College; "Atomic Structure and Valence," John A. Timm, Simmons College; "*s, p, d, f* Electrons and the Periodic Table," William F. Kieffer, College of Wooster, and Edward L. Haenisch, Wabash College.

The new Parker Cleaveland Chemistry Hall at Bowdoin was ideal to house the conference, to display the apparatus and book exhibits, to show the motion pictures, and to provide meeting rooms for the round tables. The exhibits were arranged by a committee under the chairmanship of Paul F. Davis, Bellows Falls High School, Bellows Falls, Vermont, and the motion picture and other visual aids under the chairmanship of Carl P. Swinnerton, Pomfret School, Pomfret, Connecticut. The "Down East" clambake (with lobster) was held on Wednesday, and following this, Ralph E. Keirstead, Bulkeley High School, Hartford, Connecticut, showed colored slides taken on his 18,000 mile trip to search out the natural resources of the United States, made as part of his Ford Foundation fellowship project.

Particularly memorable were the Tuesday evening illustrated lecture on "New Hampshire Wild Life" presented by Uel Gardner, of the New Hampshire State Fish and Game Department, and the Thursday evening report on a "Chemical Murder Case" by Otto Eisenchiml, Scientific Oil Compounding Company, Chicago, Illinois.

The social hours that followed the evening meetings, held in the beautiful and spacious Moulton Union Hall, were arranged under the chairmanship of Louise O. C. Swenson, English High School, Lynn, Massachusetts, and included a "Twisted Whist Party" and a "College Whist Party." John A. Timm brought up wire recordings of the Berkshire Music Festival to provide background music for the social hours.

ADJOURNED ANNUAL MEETING, AUGUST 28, 1953

The adjourned annual meeting of the NEACT was reconvened at 11:00 A.M. by the President, Dorothy W. Gifford.

The Treasurer's report was presented. An abridged statement follows:

Expenses for the year	$2648.89
Receipts	2479.99
Deficit	$ 168.90
Balance, July 1, 1952	$1385.24
New balance, June 30, 1953	1216.34
	$168.90

The deficit will be made up in part by transfer of earnings of the Endowment Fund to the general treasury. These amount to $94.99.

Leallyn B. Clapp, Secretary, presented the report of the Membership Committee.

Members who joined since the May Meeting:

Rev. Brother Marinus, CFX, Principal, Mission High School, Roxbury, Massachusetts.
Edward L. Haenisch, Chairman, Chemistry Department, Wabash College, Crawfordsville, Indiana.
Walter A. Moyer, Jr., Assistant Professor of Chemistry, Middlebury College, Middlebury, Vermont.
Carleton S. Spear, Chairman, Department of Science, New Rochelle High School, New Rochelle, New York.
Harold B. Sturtevant, Instructor, Textile Division, Rhode Island School of Design, Providence, Rhode Island.
George E. Zink, Teacher of Chemistry, Groton School, Groton, Massachusetts.

Members who joined at the Summer Conference:

John W. Beamesderfer, Head of Chemistry Department, University of Maine, Orono, Maine.
Russell W. Bennett, Fisher Scientific Company representative, Lexington, Massachusetts.
Raymond A. Bournique, Assistant Professor of Chemistry, Bowdoin College, Brunswick, Maine.
Ethel H. Dodge (Mrs. Edward), Head, Science Department, Albany Academy for Girls, Albany, New York.
Irwin H. Gawley, Jr., Chairman, Science Department, Tenafly High School, Tenafly, New Jersey.
John J. Kassay, Head, Science Department, Gardiner High School, Gardiner, Maine.
Richard W. Kunemund, Teacher of Physics, Bergan Field, New Jersey.
K. G. Stone, Associate Professor of Chemistry, Michigan State College, East Lansing, Michigan.
James L. Wolfhagen, Assistant Professor of Chemistry, University of Maine, Orono, Maine.

Summing up of membership for the year 1952–53 and through the Summer Conference:

Membership	
June 30, 1953	560
June 30, 1952	521
Resignations	10
Dropped for non-payment of dues	16
New members	
Since July 1	6
At Summer Conference	9

It was moved that a letter of appreciation be sent to all the chemistry staff of the Massachusetts College of Pharmacy for their indispensable aid in sending out the *Newsletter*. The motion passed without dissent.

President Dorothy W. Gifford presented honorary membership certificates to Ralph E. Keirstead, John R. Suydam, and Elbert C. Weaver in recognition of their value to the Association as recorded in the citations at the May 9th meeting.

President Gifford announced that the University of Massachusetts had renewed its invitation (which had to be withdrawn for 1953) and that the 16th Summer Conference would be held on the Amherst, Massachusetts, campus of that institution. New dormitory and cafeteria facilities have now made it possible for the conference to be held there. Robert D. Eddy, Tufts

College, Medford, Massachusetts, will serve as Chairman, and Edward L. Haenisch, Wabash College, Crawfordsville, Indiana, as Program Chairman.

The Secretary was instructed to express our appreciation to Bowdoin for their hospitality.

The Secretary was also instructed to send a cablegram to John Cavelti, Visiting Professor at the University of Hawaii, to express our appreciation of his difficult task as chairman of the conference *by remote control.*

NEACT MEETINGS SCHEDULED FOR 1953–54

The following meeting places and dates have been set for the divisional meetings by the Executive Committee:

272nd meeting, October 10, 1953, Spaulding High School, Rochester, New Hampshire.
273rd meeting, December 5, 1953, Brandeis University, Waltham, Massachusetts.
274th meeting, February 13, 1954, East Providence High School, East Providence, Rhode Island.
275th meeting, April 17, 1954, Avon Old Farms, Avon, Connecticut.
276th meeting, May 15, 1954, Emmanuel College, Boston, Massachusetts.

LEALLYN B. CLAPP
Secretary

NECROLOGY

CHARLES JERROLD INGALLS. The necrology committee regretfully reports the death in May, 1953, of Charles J. Ingalls of Hartford, Connecticut, a chemistry teacher at Bulkeley High School, Hartford, prior to his retirement because of ill health late in 1952. Mr. Ingalls began teaching at Bulkeley High School in 1931, but served in the Navy in World War II as a lieutenant commander and was a member of the Naval Reserve, Aviation Volunteer Unit No. 2.

Mr. Ingalls was a native of Colchester, Illinois. He was graduated from Western Academy in 1922, from Western State College, Gunnison, Colorado, with the degree of B.Ed. in 1926, and from Columbia University with the degree of M.A. in 1931. Joining the NEACT in 1934, he was on the inactive list for many years while in the service, and became active again in 1949.

PERLEY CONANT VOTER. Notice has been received of the death early in the summer of Perley Conant Voter of Middlebury College, Middlebury, Vermont. Members who attended the Summer Conference at Middlebury will recall the cordial welcome given to the NEACT by Dr. Voter and his wife and the generous hospitality accorded our members and their families on this occasion.

After graduation from Bowdoin College with an A.B. degree in 1909, he received his master's degree from Harvard University in 1918, under Theodore W. Richards, and entered the chemistry department of Middlebury College, of which for many years he served as chairman. The premedical work in chemistry was his special interest.

S. WALTER HOYT
Chairman, Necrology Committee

To the Editor:

I was very much interested in reading the paper "Aspects of isomerism and mesomerism. Part I," by Dr. Richard L. Bent [THIS JOURNAL, **30,** 220–8 (1953)]. I believe that the principles of the chemical structural theory deserve to be plainly stated and its concepts clearly defined in view of the recent criticisms of the theory of resonance in the U.S.S.R. and elsewhere. However, articles such as the one referred to above do not help us very much since they contain certain misconceptions and inconsistencies. I will give some examples of the inconsistencies to be found in Dr. Bent's paper:

(1) On page 224 it is stated that, "A molecule like benzene does not possess one electronic structure part of the time and another structure (or structures) the rest of the time." And further, "It is unfortunate that the term resonance is likely to give one the erroneous idea that some kind of a 'mechanical' oscillation is involved." However, on page 225 there is the following statement: "A mathematical treatment of the problem (the molecule H_2) has shown that the electrons, while moving about both nuclei, spend the large part of the time *between* the nuclei..." Also, on page 226 the author says that "...the electrons spend the large part of the time *between* the nuclei."

It seems, therefore, that there is a mechanical oscillation of electrons in a resonating covalent bond, whereas such oscillation does not occur in a resonating system of conjugated bonds.

(2) On page 226 we learn that, "The greater the ionic contribution to the actual state of the bond the greater will be the resonance, and the greater the strength of the bond." The very next sentence however reads as follows: "If the ionic contribution to a bond were exactly equal to the covalent contribution the resonance interaction and the resultant strength of the bond would be at a maximum."

(3) On page 226 it is assumed that the strength of a hybrid bond depends on the *number* of resonating structures. This view, which is shared by many

authoritative accounts of the theory of resonance, is a misconception which should be abandoned. Actually the strength of a bond depends on the interaction between the resonating structures [DEWAR, M. J. S., AND H. C. LONGUET-HIGGINS, *Proc. Roy. Soc.*, **A-214,** 482 (1952)].

Because of the many advantages of the molecular orbital theory over the resonance theory it is very likely that the former will eventually supplant the latter even in elementary courses. Why not begin the change now, following the path opened by C. R. Noller in his "Chemistry of organic compounds" (also THIS JOURNAL, **27,** 504 (1950))?

RICARDO DE CARVALHO FERREIRA

UNIVERSIDADE DO RECIFE
PERNAMBUCO, BRAZIL

To the Editor:

I appreciate Dr. de Carvalho Ferreira's interest in the paper on "Aspects of isomerism and mesomerism," and will attempt to answer each point raised in order.

(1) The author is, of course, painfully aware of the inadequacy of a qualitative (and brief) treatment of a highly mathematical subject, but unfortunately many of the mathematical ideas involved have not yet been translated into simple language.

My remarks concerning the hydrogen molecule were not intended to be interpreted as implying an oscillation between different electronic structures. After bond formation, the two electrons are, of course, in motion about both nuclei but the motion is not uniform so that a "piling up" of negative charge occurs between the two positive nuclei, resulting in a strong electrostatic attraction between opposite charges and in a stable molecule. Presumably such a "time-averaged" picture can be regarded as the "intermediate" electronic state (see KETELAAR, J. A. A., "Chemical Constitution," pp. 143 ff., for a recent discussion of the problem).

(2) Perhaps it should have been worded differently, as follows:

If, for example, the extreme covalent structure has the same bond-energy value as the extreme ionic structure then the two structures can be regarded as contributing equally to the "intermediate" electronic state of the molecule. The actual bond energy of such a molecule is greater than the bond energy for either structure alone, the gain being called the resonance energy of interaction. In such cases the resonance interaction will be at a maximum because if either of the extreme structures had a greater or smaller bond energy value than the other, the resonance energy of interaction would be smaller (see PAULING, L., "Nature of the Chemical Bond," p. 35).

(3) The conventional treatment of the subject was followed. While no theoretical significance was intended, it does appear that the concept of the resonance energy depending upon the number of contributing structures (of reasonable stability) is a useful rule of thumb.

I agree with Dr. Ferreira that the molecular orbital theory offers a number of advantages and that it should be incorporated into even elementary courses and texts. Nevertheless, I am convinced that the convenience and great simplicity of the resonance theory "language" is such that it will not readily be abandoned (even though it has often been misused in the past). Coulson, who has made noteworthy contributions to molecular orbital theory, has this to say in the preface of his recent book, "Valence":

". . .a serious attempt has been made to use both of the two main competing theories, usually known as the molecular-orbital and valence-bond methods. Both are approximations, whose range of validity is now sufficiently understood for us to recognize the folly of trusting to either alone."

Dr. J. Figueras, of these Laboratories, has pointed out in connection with Part III that the author was a little hasty in stating that no optically active compounds were known which involved a type of asymmetry brought about by deuterium alone. Thus, compounds such as α-deuteroethylbenzene and 3-deutero-*trans*-*p*-menthane have been shown to be optically active (see *J. Am. Chem. Soc.*, **72,** 3796 (1950) and references given there).

RICHARD L. BENT

EASTMAN KODAK COMPANY
ROCHESTER, NEW YORK

● BASIC COLLEGE CHEMISTRY

Joseph A. Babor, Professor of Chemistry, College of the City of New York. Second edition. Thomas Y. Crowell Co., New York, 1953. xvii + 766 pp. Illustrated. 15 × 22.5 cm. $5.

THE second edition of this popular text continues to feature the use of a long-type periodic table as modified by the author. In revising the book, the author states that he has tried "to maintain a suitable balance between the fundamental principles of physical chemistry essential to an elementary treatment of chemistry" and his stated purpose "to teach the chemistry of the elements and their compounds, the chemical reactions and the equations expressing the mechanisms of the changes, the qualitative relations and, above all, the explanation of the why and how of chemical reactions."

Accordingly, after presenting some general introductory material, the basic concepts of atomic structure and the periodic table are introduced in Chapters 3 and 4, followed by a chapter on the gaseous state, before the first of the elements, oxygen and hydrogen, are presented. In the first half of the book, which would probably constitute the work of the first semester, approximately two-thirds of the chapters are devoted to chemical principles. Of the 43 chapters in the text, 16 deal chiefly with chemical principles.

The author presents the material of the text in a thorough, orderly way with well selected study questions and numerical problems with their answers at the end of the chapters. A supplemental reading list at the end of each chapter gives numerous references to books and journal articles, including many to THIS JOURNAL. However, the titles of the articles are not included nor is there identification with any specific topic in the chapter.

One of the distinctive features of the text is the consistent use of the hydronium ion, H_3O^+, in place of the hydrogen ion. In the treatment of hydrolysis, cations are written in the hydrated form such as $Al(H_2O)_5OH^{++}$. He goes even further to explain that a solution of sodium carbonate is basic because the carbonate ion is stronger as a base than the hydrated sodium ion is as an acid. The explanation of the neutrality of a solution of sodium chloride states that the hydrated sodium ion, $Na(H_2O)_x^+$, is very weak as an acid and the chloride ion is very weak as a base producing equal concentrations of H_3O^+ and OH^-. The author goes further to write the reactions of water with the chloride ion as:

$$H_2O + Cl^- \leftarrow HCl + OH^-$$

Later in the book, even solubility product is introduced with the reaction of silver chloride with water:

$$Ag^+Cl^- + (x + y)H_2O \rightleftharpoons Ag(H_2O)_x^+ + Cl(H_2O)_y^-$$

although the hydrated formula is not used when the solubility product is written.

Some of the explanations used in the book seem involved and possibly confusing for a beginning course. For example, an explanation of the principles of rate of reaction presents illustrations of 16 possible ways in which "one molecule of B can combine with two molecules of A, assuming that there are present 1 mole of B and 4 moles of A."

In the explanation of the theory of the hydrogen electrode, the book states that the platinum electrode "activates" the hydrogen, transforming it into atomic hydrogen which gives up an electron to the metal and combines with a molecule of water to form a hydronium ion.

Although mercurous chloride is written as Hg_2Cl_2, the cuprous ion is written as Cu^+, and cuprous iodide as CuI. Also in the section on hydrogen fluoride, although the association of hydrogen fluoride is pointed out, the formula H_2F_2 is used consistently for its formula both as the gas and in solution, with the explanation that "since salts of the type $NaHF_2$ are known, we frequently use the formula H_2F_2 for hydrofluoric acid." No mention is made of the ring form of association, H_6F_6, in which HF can exist.

For those who have used the first edition of this text, the second edition will be welcome, with its inclusion of the recent developments in the chemical field and the "latest methods for obtaining bromine, magnesium and other important metals, silicones, rubber, atomic transformation, atomic energy and the atomic bomb." Those who are not familiar with the book will find that the author has given much thought to the orderly presentation of the chemistry of the elements, their compounds, and to the principles relating to their behavior. Especially noteworthy are the appendixes at the end of the book which contain 13 tables of useful information, a section on mathematical operations, and a four place table of antilogarithms in addition to one of logarithms.

L. REED BRANTLEY

OCCIDENTAL COLLEGE
LOS ANGELES, CALIFORNIA

● THE ATOM STORY

J. G. Feinberg. Foreword by *Frederick Soddy.* Philosophical Library, New York, 1953. vii + 243 pp. Illustrated. 14.5 × 22 cm. $4.75.

THE story is told of a diplomat who, when viewing a new-born baby for the first time, always remarked: "Well, that *is* a baby." This flattered the mother, and at the same time other mothers, within earshot, didn't complain: "Why, he didn't say that about *my* baby."

Well, this *is* a book. What more could I say without offending the scores of other authors on this subject?

To change metaphors, it is a blow-by-blow account of the battle for the bomb. No details are spared by the ringside reporter, beginning with Anaxagoras and Democritus (Round 1), down through Dalton, Avogadro, Roentgen, the Curies, Soddy, Rutherford, C. T. R. Wilson, Moseley, Aston, Cockcroft and Walton, Hahn, Lawrence, Fermi, Frisch and Meitner, to the final knockdown blows (Round 10) at Alamogordo, Hiroshima, and Nagasaki. (The decision is yet to come.) The reporting is scientifically accurate, much more so than in many similar popularizations of the atom bomb story. For this reason it is a good book for your better beginning students, for they will get the account straight, not garbled. They will also enjoy the book, because the author writes attractively; for example, page 126: "Conjecture, conjecture, conjecture! The Human Race yawned and tore the leaf marked 1938 from the calendar."

At least two chapters caught my fancy. One was a first-hand report by Sir John Cockcroft, himself, on his experiments with Walton in confirming $E = mc^2$. This piece alone justifies the printing of the book. Let us hope it sets a pattern for later reporters in getting first-hand accounts from the discoverers themselves. Another chapter is entitled A Dissertation on Nuts (the tree variety), a popular explanation: piles of walnuts, monkey nuts, filberts, different varieties, but all of the nuts weighing the same

(isobars); and, on the other hand, a single variety whose nuts weigh different amounts (isotopes). This could well be a chapter in every general chemistry textbook. (No, it wouldn't drive your students nuts.)

There are some 50 pages on the peacetime uses of atomic energy and the nuclear reactor, but nothing new or startling is revealed: how could there be? And there are 14 pages entitled Survival under Atomic Attack reprinted from a pamphlet issued by the U. S. Civil Defence (defense on this side of the Atlantic). The author might have quoted, as well, some passages from Hirschfelder's "The Effect of Atomic Weapons," instead of lulling the people to a sense of false security on how easy it is to survive an atomic attack.

Here is the work of an accurate scientist with a flair for good reporting. If you still want to read more about the atomic story you will not waste your time reading this.

HUBERT N. ALYEA

PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

● SCIENCE MAGIC

Kenneth M. Swezey. **McGraw-Hill Book Co., Inc., New York, 1952. x + 182 pp. Profusely illustrated. 15.5 × 23.5 cm. $3.75.**

LOOKING for a good birthday present for your youngster? Or some extra-class assignments for your high-school geniuses? Here is the book for you.

Most teachers are familiar with the author's previous book "After Dinner Science"; this new volume is a companion piece, equally well done, equally exciting. Happily there is more science than magic in this collection, with clear photographs and a simple discussion of the scientific principle involved in each experiment. In fact, at times I wished the results were made less obvious; it would have been much more fun to have guessed what would happen.

About 150 experiments run the gamut from scientific gadgets to magic, grouped under 17 headings such as Gravity and Balance, Fluids in Motion, Fire and Heat, Seeing is Deceiving, and Scientific Sleuthing. Gadgets include a cosmic-ray detector, an electroscope, a barometer, rain-making by cloud-seeding, and tests for identifying plastics by their odor and flame-color on burning.

Not all of the experiments are ideal. I tried my best to drive a nail through a 1-inch board (page 26) but ended up with sore fingers; and I am not inept with nails, either, having built my own house. Fortunately 30 per cent hydrogen peroxide is hard to come by, so not many youngsters will be exposed to the hazards of pages 6 and 7. With so scientific a gadget as the homemade barometer (page 53) a formal explanation of the effect of T and P on volume (1/760, 1/273, 0.36 mm. per degree) might have helped, together with the suggestion to calibrate the scale against a barometer or local weather reports.

The author stumbled into a distorted truism when (page 12) he told how James Watt found what a *strong* dray horse could pull, *added 50 per cent for good measure*, and called that one horsepower; then (page 13) continues: "Oddly enough an *average* horse, performing *average* work, develops only $^2/_3$ horsepower!" Indeed!

You will end up by doing some of the tricks yourself.

HUBERT N. ALYEA

PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

● THEORETICAL NUCLEAR PHYSICS

John M. Blatt, **Associate Professor of Physics, University of Illinois, and** ***Victor F. Weisskopf,*** **Professor of Physics, Massachusetts Institute of Technology. John Wiley & Sons, Inc., New York, 1952. xiv + 864 pp. Illustrated. 15.5 × 23.5 cm. $12.50.**

THIS book is undoubtedly one of the most important to appear in the field of nuclear physics. It contains well over 800 pages and as implied by the title it is devoted almost in its entirety to the theory of nuclear processes.

Despite the instances of brilliant achievement in explaining nuclear processes and predicting properties, nuclear theory in the main has its greatest breadth when applied on a semiempirical basis. Often a "first approximation" explanation can be formulated on fundamental grounds for a particular process but manifestly important operating laws are unknown since the theory cannot account for easily discernible variations. The theory can be maintained in a dynamic state by building upon the fundamental concepts with semiempirical correlations.

The authors of this book have maintained the goal of remaining close to knowledge based on experiment, that is, they have refrained from mathematical excursions, the results of which either cannot be checked or are known to be at variance with observation. This feature of the book makes it particularly attractive to the experimentalist. On the other hand, nuclear fission is dealt with only briefly despite the large amount of empirical data because of the absence of a cohesive theory.

This reviewer found the text clearly written, with a good choice of illustrative material, and not overburdened with mathematical development. The authors did not intend it to be light reading and some familiarity with the language and concepts of quantum mechanics is a prerequisite for understanding much of the material presented.

I. PERLMAN

UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

● ORGANIC REACTIONS. VOLUME VII

Roger Adams, **University of Illinois, Editor-in-Chief. John Wiley & Sons, Inc., New York, 1953. viii + 440 pp. 51 tables. 15.5 × 23.5 cm. $9.**

ORGANIC chemists will welcome cordially this latest volume in a series which now has achieved an international reputation for excellence. The scope and limitation of a number of important reactions have been effectively presented.

The chapters are as follows: "The Pechmann reaction," by Sethna and Phadke (58 pages); "The Skraup synthesis of quinolines," by Manske and Kulka (40 pages); "Carbon-carbon alkylations with amines and ammonium salts," by Brewster and Eliel (99 pages); "The von Braun cyanogen bromide reaction," by Hageman (65 pages); "Hydrogenolysis of benzyl groups attached to oxygen, nitrogen, or sulfur," by Hartung and Simonoff (64 pages); "The nitrosation of aliphatic carbon atoms," by Touster (51 pages); and "Epoxidation and hydroxylation of ethylenic compounds with organic peracids," by Swern (56 pages).

The editors and contributors are to be congratulated for making available this invaluable book.

HENRY GILMAN

IOWA STATE COLLEGE
AMES, IOWA

ANNUAL INDEX—JOURNAL OF CHEMICAL EDUCATION

VOLUME 30, 1953

The annual index for Volume 30 of the JOURNAL OF CHEMICAL EDUCATION is divided into several parts. Authors are listed in three sections: authors of articles, books reviewed, and letters to the editor. The subject index includes both subjects and titles to articles; the books reviewed are listed in a separate section. The principal subject entries are distinguished from titles by printing the former in italics. Portraits, including medals, are indicated by (P), frontispieces by (F).

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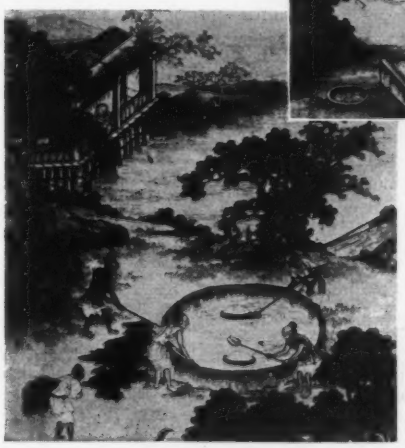

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1. Forwarding Address. Papers intended for publication in the JOURNAL OF CHEMICAL EDUCATION should be submitted to NORRIS W. RAKESTRAW, *Editor*, Scripps Institution, La Jolla, California.

2. Manuscript. The manuscript submitted should not have been published elsewhere. The work of the editorial office is facilitated and better service is assured the author when duplicate copies (the original and a carbon) are submitted. Typing of both text and references should be double-spaced, with 2–3 cm. margins. The title of the article should be followed by the name and business or institutional address of the author. If the paper has been presented at a meeting, a footnote giving name of the society, date, and occasion should immediately follow the author's name. The usual editorial customs, as exemplified in the most recent issue of the JOURNAL should be followed as closely as possible.

Galley proof of each article will be submitted to the author. This proof should be carefully corrected and returned promptly to the *Editor's Office*. Page proof will not be submitted.

3. References and Footnotes. In historical and biographical articles and in papers containing only two or three literature references it is desirable that the references be handled as footnotes. Such references should be designated by superior numbers and the reference itself should be placed in the body of the text immediately following the citation and set off by rules.

In articles of the scientific review type each reference to the literature should be designated by a number, in italics (indicated in a typescript by a single underline) and enclosed in parentheses, corresponding in size with the body of the text and set in the line of reading matter. All the references are to be assembled, arranged numerically, and placed at the end of the article under the heading, Literature Cited. The numbers in parentheses are to be placed flush with the margin and if the reference exceeds one line, the succeeding line or lines should be indented. The lists of references should be typed, double-spaced.

When specific citations of previous literature are not made but when it seems desirable to append a general bibliography, it is preferable that arrangement be made alphabetically on the basis of authors' or senior authors' names.

A reference to a periodical should include, in the order named: (1) author's name, (2) name of periodical (use of standard abbreviations designated in the "List of Periodicals Abstracted by *Chemical Abstracts*"), (3) volume number, (4) page (give exact page number at which the point cited is to be found, or if the entire article is the reference, give the page numbers inclusive), and (5) date of publication.

Example:

(1) KRAUS, C. A., AND C. L. BROWN, *J. Am. Chem. Soc.*, **52**, 3690–6 (1930).

A reference to a book should include, in the order names: (1) author's name, (2) title of book (enclosed in quotation marks), (3) edition, if more than one, (4) name of publisher, (5) address of publisher, (6) date of publication, (7) volume number, (8) pages (give exact page number at which the point cited is to be found).

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(1) COHEN, J. B., "Organic Chemistry for Advanced Students," 5th ed., Longmans, Green and Company, New York, 1928.

References to explanatory notes such as (1) occasion on which paper was delivered, (2) acknowledgments, (3) definitions of obscure or unfamiliar terms, (4) changes in address, etc., are to be designated in the text by superior numbers in sequence with other footnotes in the article. Such a footnote should be inserted as a separate line (or lines) immediately following the word to which it refers and should be separated from the text by lines.

4. Illustrations. Not all articles lend themselves to illustration, but articles which do should be accompanied by as many pertinent illustrations as possible. The best possible selection of illustrations available will be made by the editorial staff. As a rule, apparatus, particularly if complicated, is best presented by means of line or working drawings. Photographs are sometimes sufficient, however. When both can be obtained, it is generally desirable to include both with the manuscript. Unless lettering can be done by one of the mechanical devices it should be in pencil only.

Photographs should have a gloss finish and should be at least post-card size—larger, if possible. Only prints which are unblurred and which show sharp contrast between light and dark areas can be satisfactorily reproduced. Authors should exercise scrupulous care in crediting photographs which require credit.

Line drawings should be carefully prepared in *black India ink* on plain white drawing paper, blue tracing cloth, or blue-lined coordinate paper twice or three times the size desired in the printed cut; it is convenient, when permitted by the scale required, to have them the size of the manuscript.

For *graphs* coordinate paper should be printed in *blue* only, with the important coordinate lines ruled over in black; the black-ruled square should in general not be less than ten millimeters on a side; the lines of the curves should be the heaviest, except the frame; points on the curves should be indicated by true circles, not crosses. All lines, legends, numbers, and letters which cannot be set in type at the margin of the cut but must constitute a portion of the cut itself are to be so proportioned that they will be clearly legible in the cut. The numbering of the coordinate axes, the number of the figure, and any necessary explanations of the figure should be printed in pencil in the margin of the sheet, as they are usually set up in type rather than reproduced from the drawing. Typewritten designations are not black enough to reproduce satisfactorily. Where lettering cannot be done adequately, designations left in pencil can be taken care of in the editorial office.

Tables should be inserted in the body of the manuscript at the proper place.

All photographs, line drawings, and tables should be provided with self-explanatory titles or legends. Each illustration should be marked in pencil on the margin with the name of the author and the title of the article to which it refers.

Authors are invited to examine the series of articles by E. M. Hoshall entitled "Chemical Drawing" ["I. Fundamentals of chemical drawing," J. CHEM. EDUC., 11, 21–3 (1934); "II. Conventional representation of materials and equipment," *ibid.*, 11, 23–7 (1934); "III. Arrangement of drawings," *ibid.*, 11, 154–8 (1934); "IV. Charts, graphs, and diagrams," *ibid.*, 11, 235–41 (1934); "V. Photographs," *ibid.*, 11, 546–50 (1934).]

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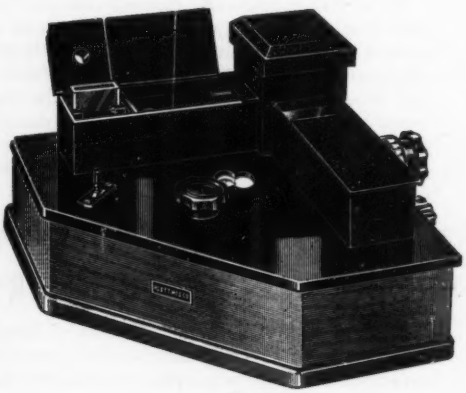

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New Radiocarbon Ring-Labeled Aromatics

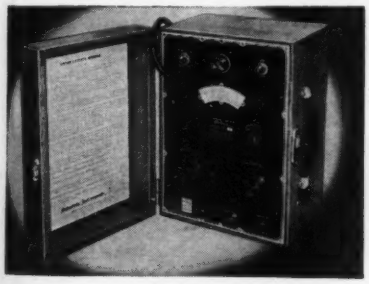
Four new ring-labeled aromatics have been added to the list of 86 radiocarbon compounds available from the Nuclear Instrument & Chemical Corp., 229 W. Erie St., Chicago 10, Illinois.

Uniformly labeled benzene, toluene, and benzoic acid are important in commercial chemistry since benzene and toluene are raw materials for industrial organics while benzoic acid is extensively used as a food preservative. Labeled benzaldehyde is a useful starting material for the synthesis of a wide variety of complex organic chemicals.

All four compounds are available in 1, 0.5, and 0.1 millicurie packages under regular A.E.C. licensing procedures. These compounds will be especially useful in fundamental studies in physical, organic, and biological science as well as in process control in industry.

Improved Conductivity Bridge

A new, improved general-purpose conductivity bridge for electrolytic conductivity and electrical test measurements is announced by Industrial Instruments, Inc., 89 Commerce Rd., Cedar Grove, New Jersey. The new instrument has been cataloged as the Type RC-16B.



It features variable sensitivity control up to a maximum of one-third of 1%. Sensitivity is regulated by means of a knob on front panel. Range of the instrument is from 0.2 to 2,500,000 ohms, with an accuracy of within 1% of measured resistance. Two bridge source frequencies are available at line frequency and 1000 c. p. s. Indicating device is an electron-ray eye tube. All components are standard types for easiest maintenance. Unit is entirely self-contained in a hardwood, self-covering, portable case. Primary power is 115 volts, a. c.

Ozone Generator

Some time ago Father J. E. Ransford, of Santa Clara College, California, sent us a suggestion for modifying the ozone generator which was described in our September, 1951, issue. He suggests using a high-vacuum leak-tester in place of the induction coil.

Hydrogen Cannon

Father Ransford (see above) also described a hydrogen cannon in our April, 1950, issue. He writes that after a Plexiglas cylinder had been substituted for the glass, the cannon withstood several hundred firings without mishap and won a first prize for the two students who demonstrated it at a Departmental exhibition.

Fire Extinguisher

A new type of fire extinguishing agent, several times as efficient as carbon tetrachloride, is now in production at Eston Chemicals Division of American Potash & Chemical Corp. The compound is methylene chlorobromide, and is commonly referred to as "CB." It was first developed in Germany during World War II, but only recently began to gain wide acceptance in this country for use in fire control equipment. In addition to efficiency it has a lower toxicity than carbon

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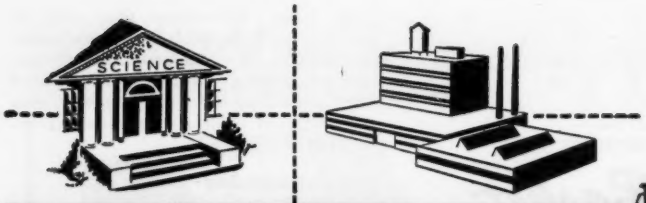

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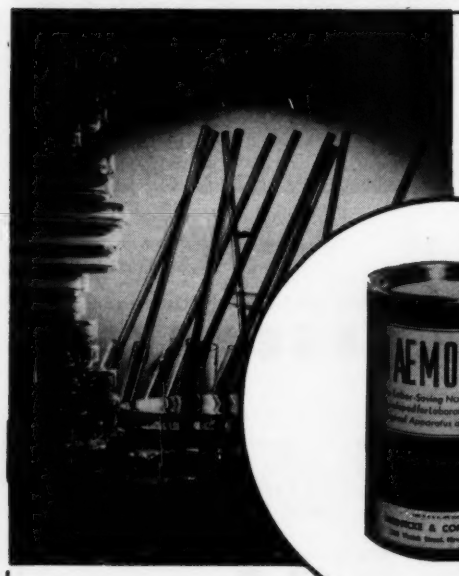

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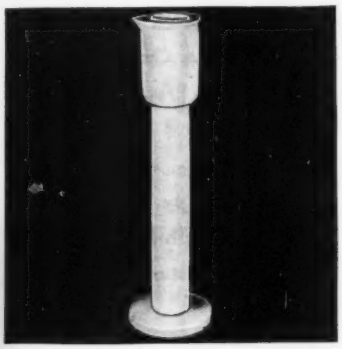
Agilene Hydrometer Cylinders

A unique hydrometer cylinder is the latest addition to the line of Agilene (polyethylene) laboratory ware manufactured by American Agile Corp., Bedford, Ohio.



In addition to being non-breakable and resistant to damage by solutions which attack glass, the cylinder shown incorporates several features which bring new safety and convenience to measurement of specific gravity of toxic or corrosive liquids.

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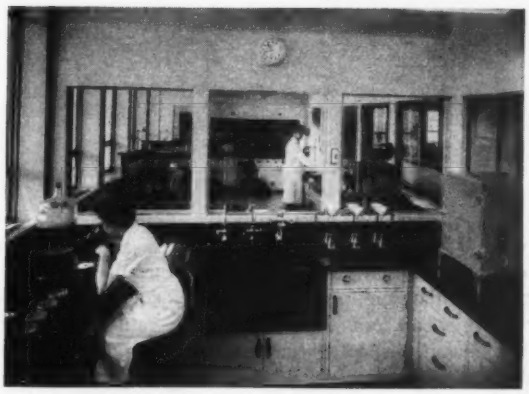

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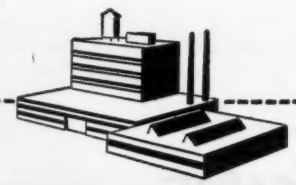

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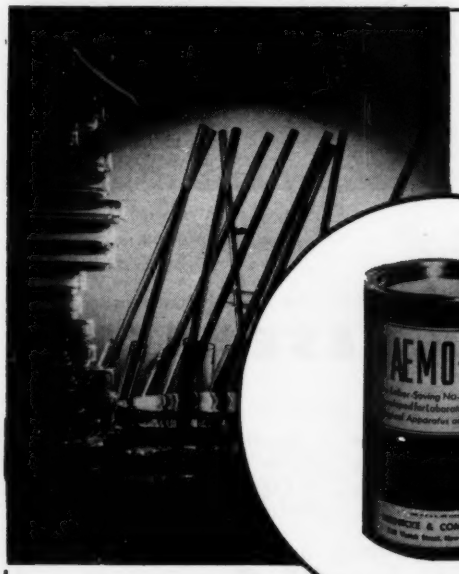

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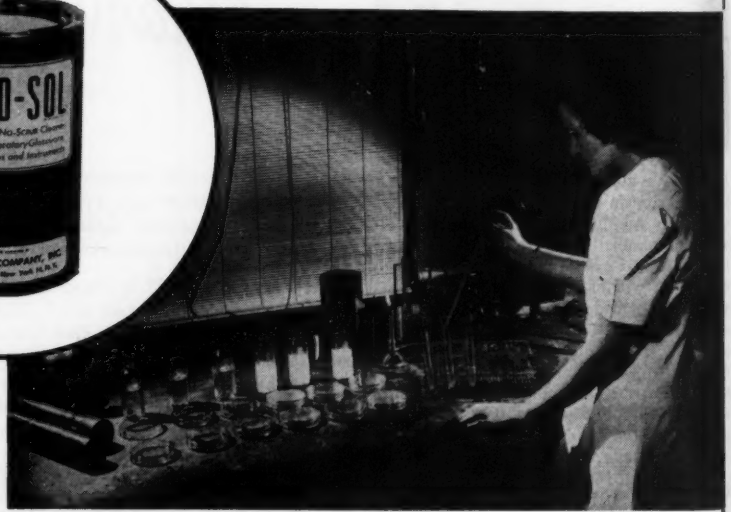

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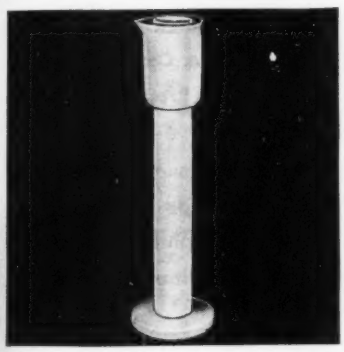

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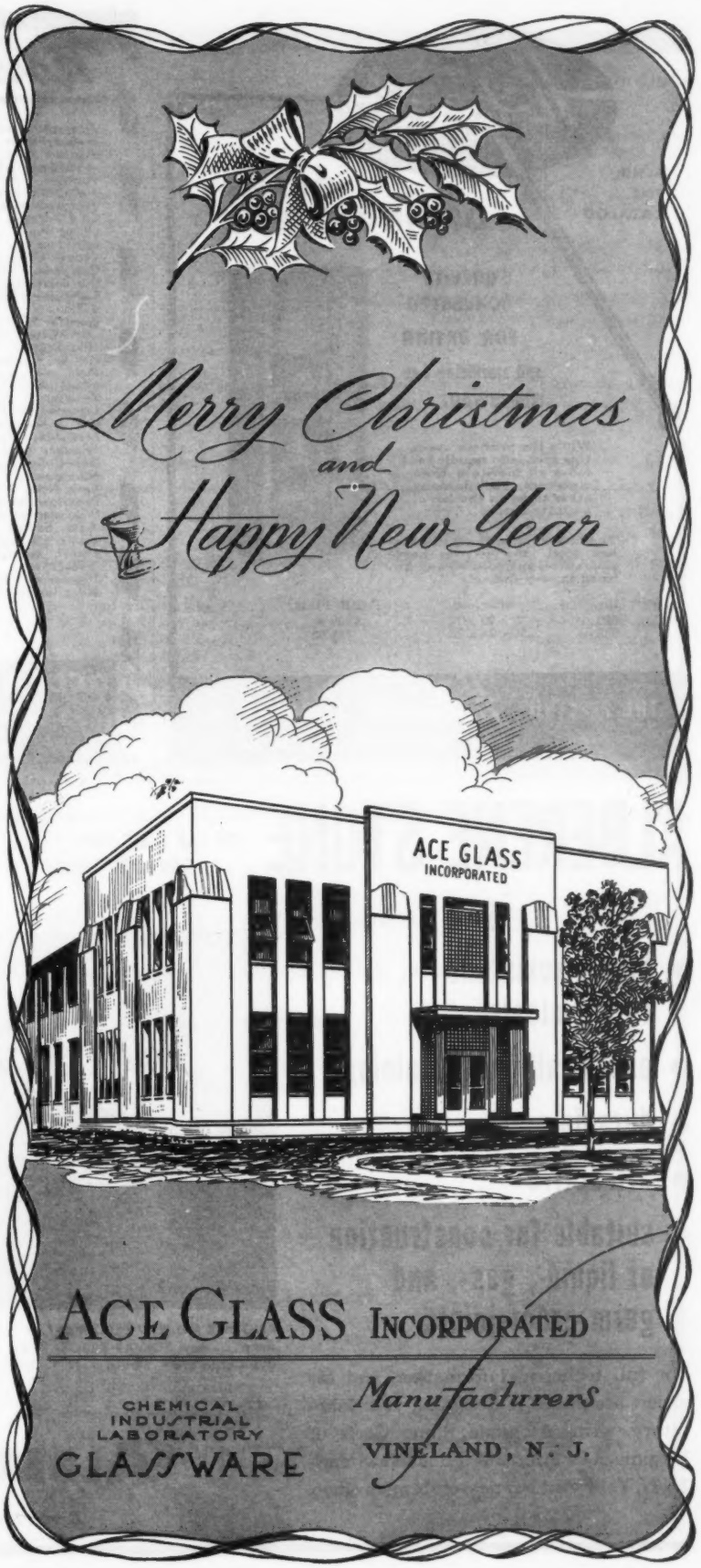

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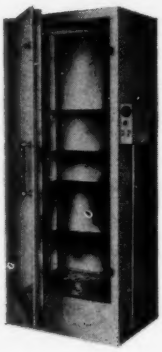

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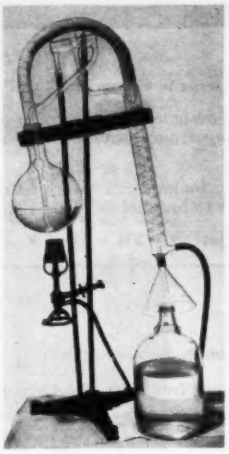

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References

(1) Ind. Eng. Chem. 25-653 (June, 1933)

(2) Ind. Eng. Chem. 25-1112 (Oct., 1933)

(3) National Bureau of Standards Journal of Research 12-241 (Feb. 1934, R.P. No. 649)

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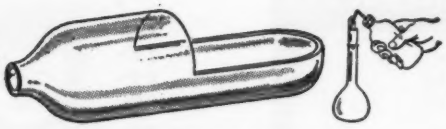

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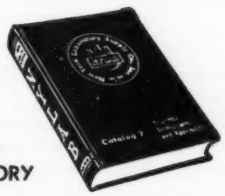

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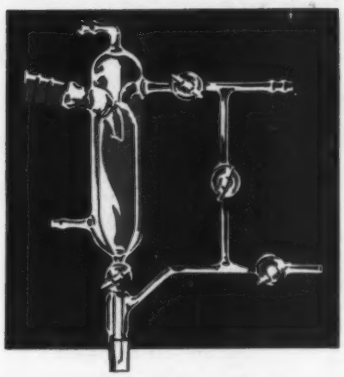

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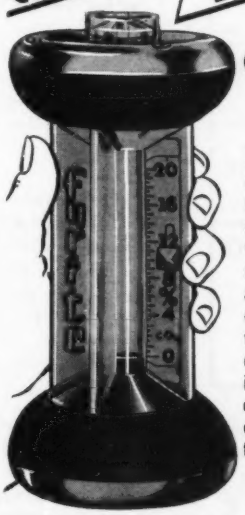

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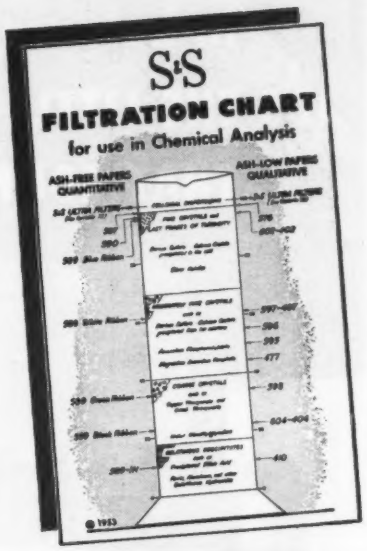

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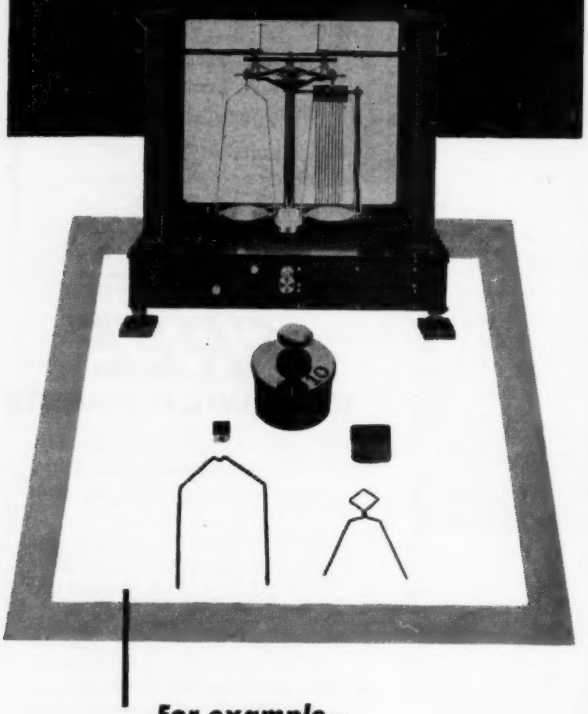

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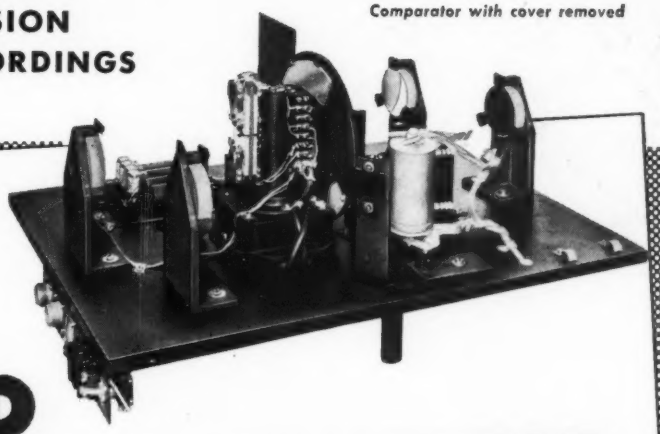

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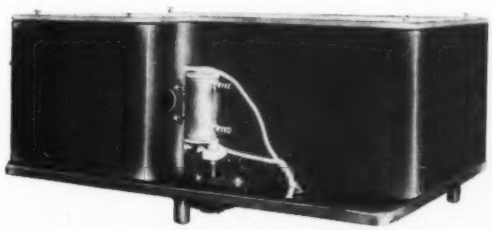

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